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A GUIDE TO THE EVALUATION OF ATMOSPHERIC ANALYZERS

California State Department of Health

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June 1973

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Intelligent selection and application of atmospheric analyzers require complete, consistent, cohesive and unequivocal information regarding the physical and performance characteristics of these instruments. This guide is designed for use by operating personnel and provides 1) definitions for selected terms in air monitoring, 2) a listing of physical and performance characteristics for which information is needed, 3) recommended criteria for operating instructions, 4) test procedures for evaluating physical and performance characteristics of air analyzers and 5) procedures for the calibration of analyzers for carbon monoxide, nitric oxide, nitrogen dioxide, ozone and oxidant, and sulfur dioxide.

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by

P.K. Mueller, Ph.D.
Y. Tokiwa
E.R. deVera
W.J. Wehrmeister
T. Belsky
S. Twiss
M. Imada

EPA Contract 68-02-0214

Project Officers

J.B. Clements, Ph.D.
T.W. Stanley

Prepared For
Environmental Protection Agency
Research Triangle Park, NC 27711

Air and Industrial Hygiene Laboratory, Laboratory Program
California State Department of Health
Berkeley, California 94704
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PREFACE

To assess air quality and to determine compliance with legally established air quality standards, noxious components such as carbon monoxide, oxidant, nitrogen dioxide, nitric oxide, sulfur dioxide, hydrocarbons and suspended particulate matter have been monitored in many areas of the country. Effective April 30, 1971, the federal Environmental Protection Agency (EPA) has promulgated primary and secondary air quality standards and regulations for all the above pollutants except nitric oxide (Federal Register, 36, No. 84, April 1971). Additional regulations (Federal Register 36, No. 158, August 1971) require the States to follow a demanding time schedule to achieve compliance with the primary and secondary standards. The regulations clearly state that these rules may not in any way be considered so as to permit deterioration of existing air quality that is already well within the confines of the standards. The federal regulations further specify that pollutants shall be measured by prescribed reference methods or methods which have been demonstrated to be equivalent to the satisfaction of EPA. This requirement indicates that equivalency with the reference procedure must be demonstrated for current and future air pollutant sampling and analysis systems.

A substantial increase in air monitoring programs is thus inevitable in order to determine short and long term trends, to assess

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the effectiveness of control programs, to substantiate compliance and to insure maintenance of existing clean air environments. Parallel to this increase in surveillance activity will be a growing demand for air monitoring instrumentation accompanied by foreseeable advances and changes in air analyzer technology. In order to deal competently with this anticipated situation, meaningful information is necessary to provide guidelines for the selection and use of air monitoring instrument including instructions on proper installation and maintenance. Only by proper application of well-tested performance evaluation procedures for air analyzers can one expect to acquire valid and reliable aerometric data.

It is therefore gratifying that EPA chose to provide our laboratory, which has decades of collective and productive experience with air pollution measurements, with resources to develop and test systematically procedures for the evaluation of atmospheric analyzer performance. It is also rewarding to realize that some results of our efforts have been included in the promulgation of federal register specifications for carbon monoxide and oxidant analyzers even before details of our work were finalized. I trust that results being produced now will be even more generally useful. Any comments regarding the utility of these procedures and deficiencies and omissions in this guide are welcome.

Peter K. Mueller, Ph.D.
Principal Investigator

June 1973

1.0 INTRODUCTION

For measuring air pollutants, a variety of commercial monitoring instruments are available. For intelligent selection and application of these instruments, reliable information concerning the physical and performance characteristics of these instruments is necessary. The information provided must be complete, consistent, cohesive and unequivocal. The terms used to describe these characteristics should be specific and well-defined. The comparison, selection and application of such instruments are enhanced when the specifications cover the same parameters and are based on uniform instrument evaluation.

To meet some of these needs, this guide, which is designed for use by operating personnel, 1) provides definitions for selected terms commonly used in the description of air monitoring practices and instrumentation, 2) lists specific physical and performance characteristics for which information is routinely needed, 3) recommends the format and information to be included in instrument operating instructions, 4) describes test procedures for evaluating physical and performance characteristics of automated analyzers for atmospheric monitoring and 5) provides procedures for the calibration of atmospheric analyzers for carbon monoxide, nitric oxide, nitrogen dioxide, ozone and oxidant, and sulfur dioxide.

2.0 MANUFACTURER'S SPECIFICATIONS

2.1 INTRODUCTION

The purpose of this chapter is to achieve uniformity by reducing the wide variations that now exists in published air analyzer specifications by delineating a list of required specifications and other pertinent information under two categories, designated here as Class I and Class II. The Class I category is intended to cover the minimum number of parameters the manufacturer should furnish so that the prospective user can judge the potential suitability of the instrument and can decide if further investigation is warranted. It is not expected to provide sufficient information to justify a purchase. Class I specifications are designed for advertisements in technical journals, product bulletins, new product flyers, and news articles.

The Class II category includes information required for complete identification and characterization of the instrument on which a decision concerning the purchase can be based. It is intended primarily for presentation in manufacturers' instrument brochures, specification sheets and instruction manuals. In all cases, manufacturers should provide realistic and accurate performance data and describe their instruments in clearly defined terms, such as those given in Chapter 10, Air Analyzer Terminology.

2.2 CLASS I

2.2.1 Instrument Description

a. Manufacturer or vendor, including address and telephone number.

b. Trade name and/or model or type.

c. Application, i.e., the pollutant the instrument is designed to measure, the intended use, such as for ambient air monitoring, industrial atmosphere monitoring, source sampling, process control, etc. The usable measurement range(s) should also be stated.

d. Measurement principle - a simple, concise term or phrase describing the principle on which the measurement is based. Inclusion of a simple logic or block diagram is helpful.

2.2.2 Installation and Operation

a. Overall physical size of the instrument (for approximate estimation of space requirements).

b. Total weight of the instrument.

c. Mobility, either portable, mobile, or stationary (see Chapter 10 for definitions).

d. Electric power requirements in terms of line voltage, current, and frequency or, in the case of battery operated units, the type of power pack used.

e. Sampling method (continuous and/or integrated). When significant, the sample flow rate should be mentioned.

2.2.3 Performance Characteristics

a. Response characteristics such as lower detectable limit, accuracy, precision, linearity, warm-up and response time.

b. Stability (drifts, thermal, vibrational).

c. Interference (list of substances and their interference equivalents).

2.3 CLASS II

The Class II includes all the information in Class I as well as certain additional information needed to assist in making a purchase decision. The additional items are listed below.

2.3.1 Instrument Description

a. Measurement principle - a detailed description of the principle on which the measurement is based. Where appropriate, diagrams and photographs should be used (see b below).

b. Drawings - block, logic, or schematic diagrams of the basic components and of the important electrical, sample, solution, and optical pathways, with an explanation of the function of each. Photographs may also be used.

c. Optional auxiliary equipment for use with the instrument.

d. Sale price of basic unit, optional equipment and accessory items.

2.3.2 Installation and Operation

a. Physical size and shape of the instrument, with space requirements for its installation, operation, and maintenance including allowances for auxiliary items and swinging space for doors and access panels.

b. Weight of each subunit making up the complete instrument.

c. Environmental requirements including the range of temperatures, humidity and, especially in the case of portable instruments, vibration conditions over which the instrument will meet stated performance specifications.

d. Air sampling requirements including sample flow rates and permissible differences in sample line pressure.

e. A list, with consumption rates, of all solutions, reagents, and gases required for start up, operation, and maintenance, but not including lubricating oils, or other materials for preventive maintenance.

f. A brief description and recommended frequency of the calibration procedure(s).

2.3.3 Performance Characteristics

a. Dynamic response including lag time, rise time, fall time, and pulse time.

b. Output signal characteristics with respect to: 1) type (electrical, mechanical, optical, etc.), 2) magnitude (voltage, current, frequency, resistance, etc.), 3) linearity (arithmetic, exponential, other function), 4) impedance, and 5) noise.

c. Audible noise.

3.0 OPERATING INSTRUCTIONS

3.1 INTRODUCTION

Most instruments require information and directions concerning their proper operation and use. To insure this, each instrument should be delivered with a manual of operating instructions. The manual should contain a section on: 1) operation and maintenance and 2) field repair or service. These sections may be separately bound.

3.2 IDENTIFICATION

The manual should be identified with the model number of the instrument and should be current for that model. Separately bound portions should be individually identified with the model number. Loose leaf manuals should have the model number appear on every leaf. Corrections or revisions should be clearly marked. Where the manual covers several models, the model number of the instrument to which it applies should be clearly indicated.

The manual should be provided with a convenient reference form listing the model number, serial number or run number, special options and modifications, location and telephone numbers of the manufacturer's representative and nearest service or repair center.

3.3 OPERATION AND MAINTENANCE SECTION

This section should provide information and instructions regarding principles, installation, initial start-up, hazards, calibration, sampling, maintenance actions, and limited trouble shooting, and should describe or contain any warranties or guarantees. Additionally, a section should be provided dealing with delivery, unpacking, and installation of the instrument. This section should be accessible to the purchaser at or before the time of delivery of the instrument and should define whether the purchaser may, in the absence of an authorized manufacturer's representative:

a. Unpack the unit
b. Install the unit
c. Operate the unit
d. Relocate the unit

The Operation and Maintenance Section should cover, but is not limited to the following topics:

3.3.1 Delivery and Unpacking Instructions

The manual should furnish details concerning shipment acceptance. A set of instructions for the orderly unpacking and inspection of the instrument should cover the following topics:

a. Unpacking

b. Warnings concerning dangers to the instrument and/or personnel during unpacking.

c. Inspection

d. Procedures to be followed when the instrument arrives in damaged condition, when parts are missing, or when wrong parts have been sent.

3.3.2 Installation and Assembly

The manual should describe the utilities and the physical environment that are required and should provide instructions for moving, mounting, and installing the instrument, including details for connecting together various components and for attachment to utilities. The following topics should be covered:

a. Electric requirements - voltage, power consumption (or current drain), frequency, number of phases, grounding.

b. Other utilities - fuel gas, hydrogen, oxygen, other gases, water, vacuum, drains. These should be qualified by specifications for the quality or purity and limitations on flow capacity and pressure.

c. Physical environment - limitations on temperature, humidity, vibration, light; requirements for shielding or isolation of the instrument; provision of exhaust vents for safety and comfort; clearance or space needed for the operation and maintenance of the instrument.

d. Working surfaces and material of construction of surroundings - floor and bench support, floor covering, bench top, bench height, supporting struts or other suggested bracing.

e. Interconnection of instrument sections and attachments to utilities - electrical, mechanical, pneumatic.

3.3.3 Hazards and Precautions

The manual should specify any hazards which could potentially injure personnel or damage the instrument. Warnings should be placed both in the manual and at appropriate locations on or in the instrument. The instrument should be equipped with, or provisions made for the attachment of, effective exhaust and effluent disposal devices. Clear instructions and warnings concerning proper disposal of any potentially hazardous discharges should be provided where appropriate on the instrument and in the manual. Tests for leaks on all lines, valves, and control devices exposed to hazardous fluids such as compressed, flammable, toxic or corrosive gases and liquids must be specified. Emergency shut-down procedures should be clearly described.

3.3.4 Application, Principle of Operation, and Scope

The manual should describe what the instrument measures, state the useful measuring range(s) and explain the principle of operation. Where appropriate, the description should include sketches, block diagrams or other pictorial representations of the instrument, the units comprising it, and the function of each. The effect of potential interferents should be described.

3.3.5 Air Sampling Requirements

The method of air sampling and any additional equipment required should be described. Where the instrument is intended for connection to an external sampling probe, the recommended probe materials, velocities and residence times, and dimensions should be specified. The preferred range of air sampling rates should be stated, and the permissible variations in sampling rate and air pressure should be given.

3.3.6 Output Signal

Most instruments are designed to be coupled with signal processing and presentation devices such as recorders, integrators, analogue and digital displays, computers, and telemetry systems. The selection of an appropriate signal processing device depends on the characteristics of the output signal from the instrument. Therefore, the manufacturer should specify the signal as to:

a. Type - mechanical, electrical, optical, acoustical

b. Characteristic - voltage, current, frequency, continuity (steady or chopped)

c. Linearity - arithmetic, logarithmic, etc.

d. Matching requirement - output impedance, resistance, back pressure. Instructions should be given for detecting and isolating response difficulties arising from mismatching of the signal source and the signal presentation device.

3.3.7 Specification

A technical summary of the instrument's physical and performance characteristics under various conditions, as well as information concerning input, output, power requirements, reagents, and utilities as listed in 2.2 and 2.3, should be provided.

3.3.8 Start-up and Operation

A precise, abbreviated summary of the operational procedures should be provided in the manual and printed on the instrument or on a permanent card affixed to the instrument. Photographs or illustrations depicting various views of the instrument including the controls suitably labeled are helpful.

Instructions for placing the unit in operation should include:

a. Procedures for procuring, preparing, and installing reagents, gases, and other consumable items.

b. Identification, purpose of and procedures for operating all controls, and adjustments.

c. Prestart-up checks

d. Step-wise start-up and shut-down procedure

e. Directions for making response checks and adjustments.

3.3.9 Calibration

Instructions and recommended frequency for precise calibration of the instrument should be provided. These should include a description of the reference method and a list of the necessary equipment and calibrating standard materials. Sources, quality, specifications, and literature references should be included where appropriate.

3.3.10 Maintenance

A routine servicing schedule should be provided. This should include a check list of inspection points and maintenance procedures, a timetable for carrying out the servicing operations, and a form for keeping maintenance and repair records.

Where the manufacturer wishes to restrict certain maintenance operations to specially qualified or authorized personnel, the nature of the qualifications or authorization should be described, the responsibilities of both the manufacturer and the purchaser should be stated clearly, and the arrangements for maintenance should be specified.

A recommended list of spare parts and subassemblies to be kept on hand should also be provided, with emphasis on those replacement items that fail frequently or are difficult to procure.

3.3.11 Troubleshooting

Check procedures to be followed in the event of instrument failure should be provided. Procedures should include instructions for disassembly and reassembly along with warnings concerning possible damage or contamination to components and steps for isolating and checking components, sections or areas to determine the probable cause of failure, and methods for remedy. This may be accomplished with a chart which outlines the symptoms, the typical cause of failure, the unit or units which may be involved, and the recommended course of action.

3.3.12 Service Information

A detailed statement regarding the manufacturer's repair policy should include:

a. Repairs which may be performed by the user or local serviceman.
b. Repairs which are to be done only by the manufacturer because they are too difficult and/or hazardous.
c. Locations and telephone number of manufacturer's repair centers.
d. Acceptable packing procedures for returning the instrument or parts thereof to the manufacturer for repair.

3.3.13 Warranty

Any guarantee or warranty should be a part of the manual and should clearly state which actions by the user will negate such warranty either completely or in part.

Availability of routine maintenance and emergency repair contracts should be stated. The manufacturer should also specify the time during which repair parts will continue to be available.

3.4 FIELD REPAIR OR SERVICE SECTION

The Field Repair or Service Section should provide detailed information to diagnose instrument failure which will permit qualified instrument servicemen to repair and restore the instrument to operation. It should include, but not be limited to, the following topics:

3.4.1 Physical Description

A general description of the physical and operational characteristics of the instrument should include:

a. A physical description of the complete instrument.

b. A diagram showing the external view with all items such as meters, knobs, switches, lights, jacks and plugs labeled.

c. A physical description of each subassembly.

d. Identification, effect of controls, and adjustments for operating, calibrating, tuning, aligning, etc., each subassembly.

e. An illustration of the interior view with the cover removed and with adequate labels for tubes, transistors, resistors, circuit boards, capacitors, photometers, cells, motors, etc. Color coding and views showing more than one level may be helpful.

3.4.2 Mechanical Description

A description of the function and operation of significant optical or mechanical units should include:

a. Diagrams of optical systems, explanations of their function, and detailed instruction for adjustment.

b. Diagrams of sampling and solution flow systems, descriptions of their operation, and procedures for calibration and adjustment.

c. Descriptions and diagrams of servo-motors, pumps, fans, circulators, heaters, etc.

d. A list of mechanical parts and acceptable commercial substitutes (if any) along with parts, numbers and descriptions.

e. A list of recommended spare parts to be kept on hand to replace those that fail frequently or that are difficult to procure.

3.4.3 Electrical/Electronic Description

A general discussion and description of the purpose and operational characteristics of each unit and subassembly should include:

a. Legible, comprehensive schematic and block or logic wiring diagrams for the power and the electronic circuits.

b. The physical location of each part in the instrument.

c. Identity of the test points to be used in making voltage, resistance, capacitance, continuity and waveform checks.

d. The voltages and waveforms expected or required between test points.

e. A list of suggested spare electrical or electronic parts to be kept on hand, especially those that are likely to fail without warning or that are difficult to obtain.

f. Warnings concerning potential hazards.

3.4.4 Major Calibration and Adjustment

Major overhaul, repair or replacement of components may cause a shift in the instrument's response which exceeds the range of normal operational adjustments. Some instruments provide wider range or coarse adjustments which can be used to compensate for such shifts. These adjustments may be locked or factory sealed to prevent unauthorized or inadvertent tampering. NOTE: The analyzer calibration should be checked with calibrating gases when changes in the coarse adjustments are made.

Procedures for major calibration and adjustment should include:

a. A list of recommended equipment, special tools, chemicals, gases, materials and standards.

b. Description and location of adjustment screws, potentiometers, trimmers, etc.

c. An explanation of the purpose for each step in the calibration procedure and directions for making necessary adjustments and response checks during calibration.

4.0 PROCEDURES FOR DETERMINING PERFORMANCE

4.1 GENERAL

4.1.1 Application

This chapter contains test procedures for determining the performance of air monitoring instruments. The procedures are designed to establish the analyzers' physical and operational characteristics such as size, measuring range, noise, lower detectable limit, drifts, lags in response, etc. Procedures for assessing the adequacy of the instruments' operating instructions are also provided.

4.1.2 Gas Generation

Suggested procedures and systems for generating the test gases required for determining analyzer performance are given in Chapter 5 (Gas Generation). To insure a stable output, the temperature of the environment surrounding the gas generation system should be maintained to within ± $1^{\circ}C$ ($2^{\circ}F$). When permeation devices are employed, the temperature of the device and the air passing over the device should be maintained within ± $0.1^{\circ}C$. The concentration of all test gases generated should be verified as directed in Step 4 of 4.1.6.

4.1.3 Test Facility Requirements

1. Conduct all tests except that for the operating temperature range at 21 ± 1°C (70 ± 2°F).

2. To assess the effect of temperature changes on analyzer performance, the test facility should be capable of providing temperatures between 4°C (39°F) and 43°C (110°) and within ± 1.0°C (2°F). An air conditioned room may be used, provided the range of temperatures required for the tests can be attained.

3. The performance of most analyzers does not appear to be affected by exposure to the range of humidities normally encountered in air conditioned environments. Control of humidity in the test environment, therefore, is not required.

4. The test facility should be sufficiently large to permit the testing of the analyzer(s) and have ample cooling capacity to absorb the heat generated by work personnel and the analyzer(s).

5. Conduct all tests except those involving response to powerline voltage at 117 ± 2 VAC and 60 ± 1 Hz.

4.1.4 Data Recording, Key Words and Symbols

1. Forms: Suggested forms for entering and recording results of the tests are shown in Tables 4-I, II and III at the end of this chapter.

2. **Keywords and Symbols**: Except as noted in Test 4.5 and 4.11, the following words and symbols are used in all equations and test procedures. For definitions of related terms, see Chapter 10, Air Analyzer Terminology.

a = intercept in the general form $Y = a + bX$

b = slope: the ratio of the analyzer output to pollutant concentration

b_m = the slope derived from the manufacturer's calibration procedure.

C = pollutant concentration (ppm, $\mu g/m^3$, etc.)

CV = coefficient of variation

FS = full scale: the maximum pollutant concentration that can be measured on a given range. It is usually specified by the instrument manufacturer.

I = interferent

IE = interference equivalent

LDL = lower detectable limit

OTR = operating temperature range

OVR = operating voltage range

ppm = the volume ($\mu\ell$) of pollutant per volume (liters) of air at the standard conditions of 25°C and 760 torr.

R = response: the instrument's output readings after conversion to concentration units ($\mu g/m^3$, ppm, etc.)

Referee method = one of the procedures in this guide used to verify the concentration of the test gas.

Span = an instrument reading or test gas concentration equal to 80 ±5% of full scale

t = time (hr, min, sec)

t_ℓ, t_{95}, t_r, $t_{-\ell}$, t_{-95}, t_f = See Test 4.11

T = temperature (°C, °F)

UO = unattended operation

X = symbol for pollutant concentration in Test 4.5

Y = reading or readout: the instrument's output in the data display units such as chart or meter readings before conversion to concentration units

$\hat{Y}$ = expected reading: the analyzer output reading expected, based on the response previously obtained with concentrations of calibrating gases.

3. Units: the concentrations for all gases are expressed as ppm (µl/ℓ). Convert ppm to µg/m^3 as follows:

$$\mu g/m^3 = \text{ppm} \times \frac{\text{mol. wt.} \times 10^3}{24.47}$$

or refer to Table 4-IX.

4.1.5 Installation and Start-up:

1. Install the analyzer(s) in the test facility described in 4.1.3 according to the instrument operating instructions. Maintain an operations log book for the analyzer and the test facility.

   Include in the analyzer log the following information in addition to the items listed in Table 4-I, Manufacturer's Data Sheet:

   a. Date of delivery
   b. Description of special options obtained with or modifications made to the analyzer
   c. Service information including the name of person to contact

d. Summary of warranty conditions and requirements

e. Record of adjustments and calibrations performed including settings of flowmeters, graduated dials, step switches, etc.

f. Record of all routine and non-routine maintenance and overhaul actions

g. Descriptions of instrument malfunctions encountered and corrective actions taken. State cause of malfunction when known.

2. Connect the output of the analyzer to a data acquisition system such as strip chart recorder, printer, digital readout, etc. When a strip chart recorder is used, the following minimum specifications are needed:

    a. Chart width - 10 inch

    b. Chart speeds - 1,2 and 5 inch/hr or
    2.5, 5 and 12.5 cm/hr

    c. Zero offset - ± 10% FS

    d. Span adjust - ± 50% FS

    e. Linearity - 0.5% FS

    f. Deadband - 0.5% FS

    g. Accuracy - ± 0.1% FS

Verify the recorder's accuracy, linearity and deadband using a millivolt potentiometer or other appropriate test equipment.

Any other type data acquisition system should be capable of providing data equal to or superior to those obtained with the recorder.

NOTE: During the operating temperature range tests, locate the data acquisition system outside the test facility.

3. Calibrate or verify all gas and reagent flows which affect analyzer response with measuring devices such as a wet test meter, dry gas meter, a calibrated rotameter for gas flows and a graduated buret, cylinder or volumetric pipet for liquid reagent flows in conjunction with a timing device such as a stopwatch.

4. Turn the instrument on. Operate for 24 hours or longer before tests are begun. The 24-hour warm-up time may be shortened when so stated in the operating instructions. For determination of warm-up time, see Test 4.15.

4.1.6 General Procedures

1. After proper warm-up and stabilization while sampling zero air, proceed with the testing. Begin recording analyzer readings when stable response has been attained. (Look for a rapid

response an apparent steady state which subsequently shifts upward or downward one or two hours later.) Inability of the analyzer to attain stable response within two hours after the start of any test except Test 4.15, Warm-Up Time, indicates possible instrument malfunction or faults in analyzer design. Discontinue testing and correct any problems before resuming the test. Consult the instrument operating instructions and/or manufacturers to resolve the problem(s). At the conclusion of each test, check the instrument response with zero air. For some tests, the zero response may be set at a level greater than zero. Average the initial and final zero responses to obtain the analyzer baseline.

Unless otherwise specified, when the difference between the initial and final baseline readings in a test is greater than 2% of full scale the test results are considered invalid and the test should be repeated.

A second invalidation indicates excessive instrument drift. Discontinue the test and correct the unit as above before resuming.

2. Set the instrument controls to provide the desired measuring range. For an instrument with multiple range selection, Tests 4.4 through 4.19 should be performed on each range. When setting the analyzer measuring range, sampling a pollutant gas concentration (span gas) is required. Refer to Chapters 6, 7, 8 and 9 for details.

3. Unless otherwise specified, set the instrument to read 5% of full scale while sampling zero air and 85% while sampling a span gas equal to 80% of full scale. This permits observation of negative responses.

4. Verify concentration of each test gas by a referee method. Collect the samples from the delivery system as close as practical to the sample intake of the instrument under test. Suggested procedures for verification are given in Chapter 5 (Gas Generation).

5. At the conclusion of each test, subtract the average zero reading from the analyzer reading Y and convert to concentration units R by dividing Y by the calibration slope b obtained in Table 4-IV as follows:

$$R = \frac{Y}{b}$$

6. Enter all results obtained in Tests 4.2 to 4.19 under the appropriate sections in Table 4-II, Column B, and in Table III.

4.2 PHYSICAL CHARACTERISTICS

4.2.1 **Definition**: the manufacturer, model, description, application, detection principle, and published performance specifications of an analyzer.

4.2.2 **Procedure**: during installation and start-up, enter the manufacturer's published information under the appropriate items in Table 4-I and in Column A of Table 4-II. For range, see Test 4.6.

1. Weight: determine the weight of each unit of the instrument and the total weight of the complete instrument.

2. Size: measure the overall dimensions of each unit of the instrument. Include all protruding items such as knobs, meters, handles, flanges, and feet which project beyond the instrument case or housing.

3. Space requirements: measure the dimensions required for the operation and maintenance of the instrument. These include the space needed for all auxiliary items and equipment such as pumps, reagent containers, and swing-out space for cabinet doors and panels.

4.3 INSTRUMENT OPERATING INSTRUCTIONS

4.3.1 Definition: a set of directions which provides information regarding the measuring principle, details of design, proper installation, application, operation, maintenance, service and repair of an analyzer. (See Chapter 3 for specifics which ought to be furnished.)

4.3.2 Procedure: based on the experiences encountered during installation and start-up, assess the operating instructions as follows:

1. Study the requirements given in Chapter 3 (Operating Instructions).

2. Inspect the operating instructions to determine which of the topics listed in Table 4-III are included.

3. Assess the adequacy and completeness of the information given for each topic in the instructions by assigning a numerical value between 0 and 10 to each topic according to the following scale.

SCORE	BASIS
0	Missing
1-2	Poor
3-5	Fair
6-8	Good
9-10	Excellent

NOTE: Assign a score of 2 to instructions that are not current. Assign a score of 1 to instructions which do not apply to the instrument designated.

4. Enter the results in Table 4-III. The maximum score is 320. In general, a score of 300 or greater is excellent, between 200 to 300 is adequate, and less than 200 is poor.

4.4 CALIBRATION

4.4.1 Definitions:

1. Calibration: the determination of the analyzer response when a series of calibrating gas concentrations are introduced to the analyzer inlet or artificial stimuli are presented to the detector.

    a. Calibration, dynamic: a performance test of the entire analyzer under simulated conditions in which the response to a calibrating gas over a known concentration range is determined. When reconciled with a static calibration, dynamic calibration also serves to verify 1) the correctness of reagent and sample air flow rates, 2) the efficiency of sample collection, 3) the integrity of the analyzer's plumbing and 4) the quality of any reagents and/or reactants.

    b. Calibration, static: the determination of the analyzer response when artificial stimuli such as standard calibrating solutions, resistors, screens, optical filters, electrical signals, are applied directly to the analyzer detector. It is a performance test for the detection and signal presentation components of the instrument and is primarily applicable to analyzers using colorimetric and conductimetric detection schemes. It is not a substitute for the dynamic calibration.

4.4.2 Procedure:

1. After proper warm-up (See Test 4.1.6, Step 1), calibrate the analyzer for each measuring range as directed in the instrument operating instructions.

2. In the absence of specific calibration instructions, use the applicable calibration procedures in Chapters 6, 7, 8 or 9.

3. Set any instrument controls so that the instrument output reads 5% of full scale while sampling zero air and reads 85% of full scale while sampling a calibrating gas equal to 80% of full scale.

4. The calibration should consist of at least six concentration levels including 0, 50, and 80 percent of full scale.

5. Plot the net instrument readings Y on the vertical axis and the pollutant concentrations C on the horizontal axis of an appropriate graph paper (rectilinear, semilog, log).

4.4.3 Calculations:

1. Use the method of least squares to determine the slope b and intercept a of the straight line that fits the data best as directed in Test 4.5.

2. The slope of the dynamic calibration curve should correspond within 10% of any static calibration curve. Differences greater than 10% indicate problems with accuracy which may be related to sampling efficiency, leaks, malfunction in the analyzer, or reagent quality. Consult the operating instructions and/or the manufacturer to solve the problem(s) before proceeding with the tests.

4.5 LINEARITY

The following procedure is designed to discriminate between linear and non-linear relationships and to determine the nature of arithmetically or exponentially linear response functions.

4.5.1 Definitions:

1. Deviation Pattern: the configuration of the differences (+ or -) of the individual calibration points from the best-fit, least square line, based on the calibration points. The pattern may be random or non-random.

2. Maximum Deviation: the absolute difference $(Y_{max} - \hat{Y})$ of the point of maximum departure from the best-fit line expressed as percent of full scale.

3. Linear Response: when the analyzer response to a series of inputs covering a specified concentration range is expressed as the equation of a straight line and the maximum deviation of the calibration

points from this line is less than 4%, the response is considered linear.

4. Non-linear Response: when the deviation pattern suggests non-random scatter of the calibration points about the best-fit calibration line and the maximum deviation observed is 4% or more, the response is considered non-linear.

4.5.2 Procedure:

1. Prepare a seven-column table as illustrated in Table 4-IV, Linearity Summary Sheet.

2. From the data collected in Test 4.4, enter the input pollutant concentrations X in column a and the corresponding analyzer readings, Y, in column b.

3. From the data in columns a and b, calculate the sums, sums of squares and sums of cross products necessary for fitting the least squares line to the calibration points. Enter the results in columns c, d and e.

4. In Table 4-V, Worksheet For Linear Relation, enter the sums from Table 4-IV and perform the operations indicated in Steps 1 through 11 to calculate the least squares line best fitting the

calibration points. This worksheet produces a line of the form:

$$\hat{Y} = a + bX$$

5. Calculate the expected reading Y predicted by the equation for each input concentration and enter the results in column f, Table 4-IV

6. Calculate the difference between the analyzer reading Y (column b) and the expected reading $\hat{Y}$ (column f) and record the positive and negative differences in column g.

7. Inspect the sequence of the +'s and -'s in column g. Assess the general pattern of the sequence. This pattern can be:

   a. a random series of positive and negative values, e.g., +-++--+, suggesting a linear function.

   b. negative, positive, then negative, e.g., --+++-- suggesting a convex function.

   c. positive, negative, followed by positive, e.g., ++---++, suggesting a concave function.

8. Select the largest value Y_{max} from column g ($Y_{max} - \hat{Y}$). Calculate the maximum deviation as % of full scale (FS):

$$\text{Max dev} = \frac{(Y_{max} - \hat{Y}) \times 100}{FS}$$

4.5.3 Determination of Linearity

1. Inspect the results for the deviation pattern and maximum deviation obtained in Steps 7 and 8 above.

2. When the response is linear, proceed to Step 5 below.

3. When the response is non-linear, logarithmic transformation of the concentration and/or the response readings may yield a linear function. Log-linear response patterns may be of the forms:

   $$\log Y = a + b \log X \qquad \text{(logarithmic)}$$

   and

   $$\log Y = a + b X$$

   or (semi-logarithmic)

   $$Y = a + b \log X$$

   To test these possibilities, convert the values in columns a and/or b of Table 4-IV to their logarithms and proceed with Steps 3 through 8 of 4.5.2.

4. When the results still suggests the response is non-linear, place a check mark in the square designated "non-linear" in Table 4-IV and

enter the word "non-linear" and a dash for "maximum deviation" in column B of Table 4-II.

NOTE: Due to the wide variety of relationships possible, the derivation of equations that fit hyperbolic and transcendental relationships are usually not feasible. Such relationships may be represented by graphically fitting the best line through the calibration points. The resulting curve may then be used as a template to transform the net analyzer reading to concentration.

5. A linear relationship exists when the maximum deviation is less than of 4% or when there is a random deviation pattern.

6. Based on the conclusions from Step 5 above, place a check mark in the appropriate square (linear, non-linear or linear with poor precision) in Table 4-IV and enter the corresponding term and maximum deviation value in column B of Table 4-II.

4.6 MEASURING RANGE

4.6.1 Definition: the nominal minimum and maximum concentrations which the instrument is capable of measuring. Many analyzers provide multiple range selection capability for greater accuracy and ease of interpretation. Range is usually specified by stating the lower and upper pollutant concentrations that can be measured, as for example 0 to 1 ppm or 0 to 5 ppm.

4.6.2 **Procedure**: Record the manufacturer's stated measuring range in concentration units in column A, Table 4-II by stating the lower limit first, then the upper limit: e.g., 0 to 1 ppm, 0 to 10 ppm. For instruments with multiple range selection, record all ranges. No test is required.

4.7 CALIBRATION ACCURACY

This test applies to instruments calibrated according to the manufacturers' procedures and for those the manufacturers state no calibration is required.

4.7.1 **Definition**: the deviation between the slope b_m of the curve obtained by the manufacturer or with his calibration procedure and the slope b obtained with a calibrating gas. It is expressed in percent.

4.7.2 **Procedure**:

1. From the manufacturer's calibration, determine the slope b_m using the procedure described in Test 4.5.

2. Compare b_m with the slope b obtained in Test 4.5.

4.7.3 **Calculation**:

1. Calculate the accuracy in percent as follows:

$$\text{Accuracy, \%} = \frac{b - b_m}{b_m} \times 100$$

2. Enter the result in column B of Table 4-II.

4.8 DRIFT AT ZERO

4.8.1 Definition: the deviation in analyzer output during a stated time period, usually 24 hours, of unadjusted continuous operation when sampling zero air. It is expressed in percent of full scale.

4.8.2 Procedure:

1. After proper warm-up (See 4.1.6, Step 1) on zero air, record the reading Y_o and the time t_o.

2. Continue sampling zero air for 24 hours. Make no manual adjustments to the electronic and/or gas and reagent flows during this test. Automatic adjustments which are a part of the normal instrument operation are permitted.

3. Determine and record the reading Y_m when the maximum departure from the baseline occurred and the reading Y_{24} at the end of 24 hours.

4. For instruments with multiple range selection, repeat Steps 1 through 3 for each range.

4.8.3 Calculations:

1. Convert Y_o, Y_m and Y_{24} to concentration units R_o, R_m and R_{24} as directed in Step 5 of 4.1.6.

2. Calculate the maximum zero drift in percent of full scale and the drift at the end of 24 hours as follows:

a. $$\text{Max zero drift, \%} = \frac{R_m - R_o}{FS} \times 100$$

b. $$\text{24 hr zero drift, \%} = \frac{R_{24} - R_o}{FS} \times 100$$

c. Enter the results in Table 4-II. Report values less than twice the noise as zero (see Test 4.10 for noise at zero).

4.9 DRIFT AT SPAN (80% FULL SCALE)

4.9.1 Definition: the deviation in analyzer output during a stated time period, usually 24 hours, of unadjusted continuous operation when sampling a span gas equal to 80% of full scale. It is expressed as percent full scale.

4.9.2 Procedure:

1. After proper warm-up (See 4.1.6, Step 1) on zero air, record the zero baseline reading Y_o. Generate a pollutant test gas equal to 80 ± 5% of full scale. Verify the pollutant concentration C_{80} by

the referee method specified in Chapter 5, Table 5-II. Switch the analyzer inlet to sample the test gas. Sample until the instrument reading indicates a stable reading Y_{80} at the test gas concentration. At this time, start and record the time t_o.

2. Continue to sample for 24 hours. Make no manual adjustments to the electronics, gas or reagent flows during this test. Automatic adjustments which are part of the normal instrument operation are permitted.

3. At the end of the 24 hour test period, verify the pollutant concentration as in Step 1 above and switch the inlet to sample zero air.

4. Determine and record the reading Y_m when the maximum departure from Y_{80} occurred and the reading Y_{24} at the end of 24 hours.

5. For instruments with multiple range selection, repeat Steps 1 through 4 for each range.

4.9.3 Calculations:

1. Convert Y_{80}, Y_m and Y_{24} to concentration units R_{80}, R_m and R_{24} as directed in 4.1.6, Step 5.

2. Calculate the maximum drift in percent of full scale and the drift at the end of 24 hours as follows:

a. $$\text{Max span drift, \%} = \frac{R_m - R_{80}}{FS} \times 100$$

b. $$\text{24 Hr span drift, \%} = \frac{R_{24} - R_{80}}{FS} \times 100$$

c. Enter the results in Table 4-II. Values less than twice the noise are reported as zero (see Test 4.10 for noise at span).

4.10 NOISE

4.10.1 Definition: unwanted, spontaneous, short-term variations in analyzer response about the mean output, not caused by variations in pollutant concentration. It is expressed as percent of full scale.

4.10.2 Procedure:

1. Noise at zero:

   a. Examine the analyzer readings during the first 30-minute interval from the data in Test 4.8. Select the maximum reading Y_1 and the minimum reading Y_2 during this period.

   b. Convert Y_1 and Y_2 to concentration units R_1 and R_2 as directed in 4.1.6, Step 5.

c. Calculate the noise at zero in percent of full scale as follows:

$$\text{Noise at zero, \%} = \frac{R_1 - R_2}{FS} \times 100$$

d. Enter the result in Table 4-II.

e. For analyzers with multiple range selection, determine the noise at zero for each range.

2. Noise at 50%

a. After proper warm-up (See 4.1.6, Step 1) on zero air, generate a pollutant test gas concentration equal to 50 ± 5% of full scale. Switch the analyzer inlet to sample the test gas. Verify the pollutant concentration and record the reading Y_{50} when a stable reading is obtained.

b. Continue to sample for one hour. Examine the readings during the first 30 minutes from the one-hour period. Select the maximum reading Y_1 and the minimum reading Y_2 during this interval.

c. Convert Y_1 and Y_2 to concentration units R_1 and R_2.

d. Calculate the noise at 50% of full scale in percent of full scale as follows:

$$\text{Noise at 50\% of FS} = \frac{R_1 - R_2}{FS} \times 100$$

e. Enter the result in Table 4-II.

f. For analyzers with multiple range selection, determine the noise at 50% on each range.

3. Noise at Span:

   a. Examine the readings during the first 30 minutes from the data in Step 2 of Test 4.9.2. Select the maximum reading Y_1 and minimum reading Y_2.

   b. Convert Y_1 and Y_2 to concentration units R_1 and R_2.

   c. Calculate the noise at span as follows:

$$\text{Noise at span} = \frac{R_1 - R_2}{FS} \times 100$$

   d. Enter the result in Table 4-II.

   e. For instruments with multiple range selection, determine the noise at span for each range.

4.11 PRECISION AND RESPONSE TIMES

The tests for determining time delays in analyzer response (lag, rise, fall, etc.) are conducted in conjunction with the measurement of precision.

4.11.1 Definitions:

1. Precision: the variability in repeated measurements of the same pollutant concentration expressed as the coefficient of variation, i.e., the standard deviation of the individual results expressed as a percent of the mean.

2. Response Times (See Figure 10-I)

   a. Lag time (initial response time), t_ℓ: the interval between the time t_o, when a step change (increase or decrease) in pollutant concentration is made, to the time t_1 when the instrument indicates a response equal to twice the noise.

   $$t_\ell = t_1 - t_o$$

   b. Time to 95%, t_{95}: the interval between the time t_o, when a step increase in pollutant concentration is made, to the time t_{95} when the instrument indicates a response equal to 95% of the step change.

$$t_{95} = t_{95\%} - t_o$$

Similarly, t_{90} corresponds to the time to indicate 90% and t_{100} the time to indicate 100% of the step change.

c. Rise time, t_r: the interval between the time to 100% (t_{100}) and the lag time (t_ℓ).

$$t_r = t_{100} - t_\ell$$

d. Time to -95%, t_{-95}: the interval between the time t_o when a step decrease in pollutant concentration is made to the time $t_{-95\%}$ when the instrument indicates -95% of the step change.

$$t_{-95} = t_{-95\%} - t_o$$

Similarly, t_{-90} corresponds to the time to indicate -90% and t_{-100} the time to indicate -100% of the step change.

e. Fall time, t_f: the interval between the time to -100% (t_{-100}) and the lag time (t_ℓ). Fall time is not necessarily equal to rise time.

$$t_f = t_{-100} - t_\ell$$

4.11.2 Procedure:

Note: For this test, a timing device is required with a resolution of at least 0.1 second, such as a watch with a sweep second hand or a stopwatch.

1. After proper warm-up (See 4.1.6, Step 1), sample zero air until a stable baseline concentration R_o (after conversion from reading Y) is recorded.

2. Generate a test gas equal to 50 ± 5% of full scale. Switch the instrument inlet from the zero gas line to the test gas line. (NOTE: Some instruments are equipped with controls for switching from sampling ambient air to sampling zero air. These should not be used for determining response times as they may introduce additional lag times which are not part of normal operation.) Verify the pollutant concentration C_{50} and note the instrument response R_{50}. Switch the instrument inlet to sample zero air.

3. When a stable response on zero air is obtained, switch the inlet to sample the test gas and begin the time t_o(up) by starting the timer or noting the time.

4. When the analyzer indicates a change in response equal to twice the noise (see Step 1 in Test 4.10.2 for noise at zero), note and record the time t_1.

5. Similarly, note and record the times t_{95} and t_{100} when the instrument indicates 95% and 100% of R_{50}.

6. Switch the inlet to sample zero air and begin the time t_o(down) by starting the timer or noting the time.

   Similarly record the times for the analyzer to indicate a change equal to twice the noise (t_i) and the times to reach -95% (t_{-95}) and -100% (t_{-100}) of R_{50}. Note: See Step 2 in Procedure 4.10.2 for noise at 50% FS.

7. Repeat Steps 3 through 6 nine more times.

4.11.3 Calculations:

1. Response Times:

   a. From the data in Steps 3 through 7, determine the time intervals required for the instrument to respond to a step increase in concentration for each trial as follows:

      Lag time up, $t_\ell = t_i - t_o(\mathrm{up})$

      Time to 95%, $t_{95} = t_{95\%} - t_o(\mathrm{up})$

      Time to 100%, $t_{100} = t_{100\%} - t_o(\mathrm{up})$

Rise time, $t_r = t_{100} - t_\ell$

b. Record the values in Table 4-IV.

c. Conversely, determine the time intervals required for the instrument to respond to a step decrease in pollutant concentrations for each trial as follows:

Lag time down, $t_{-\ell} = t_i - t_o$(down)

Time to -95%, $t_{-95} = t_{-95\%} - t_o$(down)

Time to -100%, $t_{-100} = t_{-100\%} - t_o$(down)

Fall time, $t_f = t_{-100} - t_{-\ell}$

d. Record the values in Table 4-VI.

e. Perform the operations indicated in Table 4-VI and determine the mean time and coefficient of variation for each response time characteristic. Enter the results in Table 4-II.

2. Precision:

Perform the operations indicated in Table 4-VII and determine the coefficient of variation CV at 50% of full scale. Enter the results in Table 4-II.

4.12 PULSE TIME

4.12.1 Definition: the minimum time a pollutant concentration must persist for the analyzer to register a peak response equal to the pollutant concentration (See Figure 10-II).

4.12.2 Procedure:

1. After proper warm-up (See 4.1.6, Step 1) on zero air, record the zero baseline response R_o.

2. Generate a test gas equal to 50 ± 5% of full scale. Switch the analyzer inlet to sample the test gas and record the time t_o. Continue timing and record the time $t_{100\%}$ when the instrument indicates 100% of R_{50}.

3. Switch the inlet to sample zero air. From the data in Step 2, determine t_{100}:

$$t_{100} = t_{100\%} - t_o$$

4. Switch the inlet to sample the test gas and record the time t_o. Continue sampling for a period equal to 90% of t_{100} and quickly switch the inlet to zero air. The peak instrument reading may be equal to or less than R_{50}.

5. When the reading is less then R_{50}, repeat Step 4 but increase the sampling time. This time can be approximated by interpolating between t_{90} and t_{100}. Repeat Step 4 until the minimum sampling time t_{min} for the analyzer to indicate R_{50} is obtained.

6. When the reading in Step 4 equals R_{50}, repeat Step 4 but reduce the sampling time by increments of 10% of t_{100} until a response of less than R_{50} is obtained. Repeat Step 5 above until t_{min} is obtained.

4.12.3 Calculations:

Determine the pulse time t_p from the data in Steps 5 and 6 as follows:

$$t_p = t_{min} - t_o$$

Enter the results in Table 4-II.

4.13 LOWER DETECTABLE LIMIT

4.13.1 **Definition**: the smallest pollutant concentration which produces a signal equal to twice the noise. It is expressed in concentration units.

4.13.2 Procedure:

1. After proper warm-up (See 4.1.6, Step 1) on zero air, record the zero baseline response R_o. Obtain the noise at zero from the data in Step 1 of 4.10.2.

2. Generate a test gas concentration equal to between 5 and 10% of full scale. Switch the inlet to sample the test gas. Verify the pollutant concentration C and record the response R.

3. Based on the response R, calculate the approximate concentration C_m which will produce a response R_m equal to twice the noise. Adjust the pollutant and/or diluent gas flowrates to produce this concentration. Continue to sample and note the analyzer response.

4. When the response R_m obtained in Step 3 is greater than twice the noise, decrease the pollutant concentration C_m stepwise until a response equal to twice the noise is obtained.

5. Conversely, when the response R_m obtained in Step 3 is less than twice the noise, increase the concentration C_m stepwise until a response R_m equal to twice the noise is obtained.

4.13.3 Calculations:

From the data in Steps 4 or 5 above, enter the smallest concentration C_{min} that produced a response equal to twice the noise in Table 4-II as the lower detectable limit (LDL).

$$LDL = C_{min}$$

4.14 ANALYZER DEADBAND

4.14.1 Definition: the range, in percent of full scale, through which the pollutant concentration may be varied without initiating a response equal to or greater than twice the noise. (The term deadband is commonly applied to servo-systems such as recorders but can be applied to continuous analyzers as well.)

4.14.2 Procedure:

1. After proper warm-up (See 4.1.6, Step 1) on zero air, record the zero baseline response R_o.

2. Generate a test gas equal to 50 ± 5% of full scale. Switch the analyzer inlet to sample the test gas. Verify the pollutant concentration C_{50} and record the response R_{50}.

3. Increase the test gas concentration to 65 ± 5% of full scale by varying the pollutant and/or diluent gas flowrates. Verify the pollutant concentration C_{65} and record the analyzer response R_{65}.

4. Obtain the noise at 50% FS from the data in 4.10.2, Step 2.

5. By interpolating between R_{50} and R_{65}, determine the concentration C_1 that will produce an increase in response (ΔR) from R_{50} equal to twice the noise. Generate concentration C_1 as in Step 3 above. Note the instrument response. The change from R_{50} should be equal to twice the noise. If not, repeat the procedure but adjust the concentration so that the analyzer produces a change in response equal to twice the noise.

6. Restore the test gas to the concentration C_{50} as used in Step 2 and record the response R_{50}.

7. Repeat Steps 3, 4, and 5 using a test gas concentration equal to 35 ± 5% of full scale. Verify the pollutant concentration C_{35} and similarly determine the concentration C_2 that will produce a decrease in response from R_{50} equal to twice the noise.

4.14.3 Calculations: determine the analyzer deadband in percent of full scale as follows:

$$\text{Analyzer Deadband, \%} = \frac{(C_1 - C_2)}{FS} \times 100$$

Enter the results in Table 4-II.

4.15 WARM-UP TIME

4.15.1 Definition: the elapsed time necessary after start-up for the analyzer to meet performance specifications when it has been shut down for at least 24 hours.

4.15.2 Procedure:

1. After proper warm-up (See 4.1.6, Step 1) on zero air, record the zero baseline response R_o.

2. Generate a test gas equal to 50 ± 10% of full scale. Switch the analyzer inlet to sample the test gas. Verify the pollutant concentration C_{50} and record the instrument response R_{50}.

3. Switch the inlet to sample zero air. When a stable response is obtained, turn the instrument off for at least 24 hours. Continue generation of the test gas.

4. Restart the analyzer, switch the inlet to the test gas and record the time t_o.

5. Record the time t when a stable response at R_{50} is obtained. (Precaution: Watch for a rapid response to an apparent steady state reading which subsequently shifts upward or downward within an hour or two later to a new stable reading.)

4.15.3 Calculations: determine warm-up time t_w as follows:

$$t_w = t - t_o$$

4.16 INTERFERENCES

4.16.1 Definition:

1. Interference equivalent IE: that portion of the indicated pollutant concentration caused by the presence of an interferent. It is expressed as the ratio, in percent, of the indicated concentration R_i with respect to the concentration of interferent C_i.

2. Interferent: a substance or condition other than the one being measured which modifies or perturbs the output of an analyzer.

3. Prefilters: filters or scrubbers designed to remove interferents. These are used by some air analyzers to increase the specificity of detection.

4.16.2 Procedure:

1. General: Test atmospheres containing interferents are generated by mixing each interferent with the pollutant. The interferents and their concentrations to be used for most of the currently available detection methods are listed in Table 4-VIII. Procedures for verifying their concentrations are given in Table 5-II in Chapter 5. Tests with interferents known to react in the gas phase with the pollutant are conducted in the absence of the pollutant. The addition of the interferent to the gas system should not alter the pollutant concentration.

2. Prefilters: Any prefilters should be replaced or serviced as directed in the instrument's operating instructions. In addition, the instrument should sample an interferent concentration equal to the value specified in Table 4-VIII through the prefilter for at least six continuous hours.

3. Test Gases:

   In addition to the zero air (Z) for analyzer warm-up, generate three test gases:

   a. P = flow of zero air containing pollutant which when mixed with I or A will produce the desired pollutant test concentration.

   b. I = flow of interferent gas required to produce the interferent concentration specified in Table 4-VIII when mixed with P.

   c. A = flow of zero air equal to flow I.

   To permit measurement of negative responses, adjust the analyzer zero baseline, if possible, to read 10% of full scale.

4. Test Procedure Without Pollutant:

   a. After proper warm-up (See 4.1.6, Step 1) of the analyzer on zero air, record the baseline response R_o.

   b. Generate P (containing no pollutant) and I. Mix P with I. Switch the analyzer to sample the gas mixture. Verify the interferent concentration C_i and record the response R_i.

   c. Switch the analyzer to sample zero air Z. Record the response R_o.

5. Test Procedure with Pollutant (Omit if interferent and pollutant cannot be mixed):

   a. Generate and mix P and A to produce a pollutant concentration equal to 50 ± 5% of full scale. Switch the analyzer to sample the test gas. Verify the pollutant concentration C_p and record the response R_p.

   b. Generate I and substitute for A to produce the interferent concentration C_i used in Step 4b above. Record the response R_{pi}.

4.16.3 Calculations:

Determine the interference equivalent IE at pollutant concentration C_p

as follows:

$$\text{IE (when } C_p = 0) = \frac{R_i - R_o}{C_i} \times 100$$

$$\text{IE (when } C_p \neq 0) = \frac{R_{pi} - R_p}{C_i} \times 100$$

4.17 OPERATING TEMPERATURE RANGE

4.17.1 Definition: the range of ambient temperatures through which the analyzer will meet performance specifications.

4.17.2 Procedure:

1. Install and operate the analyzer in the test facility (4.1.3). Set the test facility controls to provide a temperature (T_{21}) of 21 ± 1°C (70 ± 2°F). Verify the temperature with an appropriate temperature measuring instrument such as a laboratory mercury thermometer.

2. After the analyzer is properly warmed up (See 4.1.6, Step 1) on zero air, record the zero baseline response R_o.

3. Generate a test gas concentration equal to 50 ± 5% of full scale. Switch the analyzer inlet to sample the test gas. Verify the pollutant concentration C_{50} and record the response R_{21}.

4. Reset the test facility controls to provide the lowest possible temperature T_4 at or above but not lower than 4°C (39°F).

5. Continue to operate the analyzer until a stable response is obtained. Record the analyzer response R_4.

6. When the difference between R_{21} and R_4 is equal to or less than twice the noise, record the temperature T_4 and proceed to Step 9 below.

7. Conversely, when the difference is greater than twice the noise, estimate the temperature T_ℓ at which the change in response will equal twice the noise by interpolation between T_{21} and T_4.

8. Reset the test facility controls to provide the temperature equal to T_ℓ. Continue to sample as in Step 5 above and note the analyzer response. Repeat Steps 6, 7 and 8 until the temperature T_ℓ that causes a change in response equal to twice the noise is obtained.

9. Restore the temperature of the test facility to T_{21}. Continue to sample as in Step 5 until a stable response at R_{21} is obtained.

10. Reset the test facility controls to provide a temperature T_{43} as high as possible, but not exceeding 43°C (110°F). Follow the procedures in Steps 5 through 8 and similarly determine the upper temperature T_h which will produce a change in response equal to twice the noise.

4.17.3 Calculations:

Report the operating temperature range OTR by stating the lower temperature T_ℓ and the upper temperature T_h at which the changes in response were equal to twice the noise.

$$OTR = T_\ell \text{ to } T_h$$

4.18 OPERATING VOLTAGE RANGE

4.18.1 Definition: the range of powerline voltages through which the analyzer will meet performance specifications.

4.18.2 Procedure: This test is conducted by first determining the analyzer response to a decrease in voltage (from 117 VAC) and second by determining the response to an increase in voltage.

1. Install a variable transformer between the source of electrical power and the analyzer. The transformer should have an adjustable output between 0 and 140 VAC and be capable of delivering the amperage requirement of the analyzer.

2. Set the transformer to provide 117 ± 1 VAC. Verify this voltage V_{117} and all subsequent test voltages with a voltmeter.

3. After proper analyzer warm-up on zero air, record baseline response R_o.

4. Generate a test gas concentration equal to 50 ± 10% of full scale. Switch the analyzer to sample the test gas. Verify the pollutant concentration C_{50} and record the analyzer response R_{117}.

5. Set the transformer to provide 90 V (V_{90}). Continue to sample until a stable response is obtained and record R_{90}.

6. Determine the difference between the response R_{117} and R_{90}.

   a. When the difference is equal to or less than twice the noise, record V_{90} and proceed to Step 9 below.

   b. When the difference is greater than twice the noise, estimate the voltage V_{ℓ} at which the change in response will equal twice the noise by interpolating between V_{117} and V_{90}.

7. Reset the transformer to provide V_{ℓ}. Continue to sample as in Step 5 until a stable response is obtained. Repeat Steps 6a and 6b until the voltage $V_{\ell x}$ that produces a change in response equal to twice the noise is obtained. Record $V_{\ell x}$.

8. Restore the transformer to V_{117}. Sample as in Step 5 until a stable response at R_{50} is obtained.

9. Adjust the transformer to provide 130 VAC (V_{130}). Continue to sample the test gas and determine R_{130} as in Step 5 above.

10. Determine the difference between the response R_{117} and R_{130}.

   a. When the difference is equal to or less than twice the noise, record V_{130} and proceed to 4.18.3.

   b. When the difference is greater than twice the noise, similarly determine the highest voltage V_{hx} which will produce a change in response equal to twice the noise as in Steps 6 and 7.

11. Repeat Step 8.

4.18.3 Calculations:

Report the operating voltage range OVR by stating the lower voltage (either V_{90} or $V_{\ell x}$) first, and then the upper voltage V_{130} or V_{hx}, e.g.,:

$$OVR = 90 \text{ to } 130 \text{ V}$$

4.19 UNATTENDED OPERATION

4.19.1 **Definition**: the period of time during which the analyzer can be expected to operate unattended within the specifications.

4.19.2 Procedure:

Start this test with the maximum amount of consumable items (reagents, gases, chart paper, etc.) recommended in the instrument operating instructions. No manual adjustments to the electronic, gas or reagent flows are permitted during this test. Automatic adjustments which are a part of normal instrument operation are permitted at any time.

1. After proper analyzer warm-up (See 4.1.6, Step 1) on zero air, record zero baseline response R_o.

2. Generate a test gas concentration equal to 80 ± 5% of full scale. Switch to sample the test gas. When a stable response is obtained, verify the pollutant concentration C_{80} and record the response R_{80} and the time t_o.

3. Switch the analyzer to sample ambient air, but continue to generate the test gas.

4. At the end of 25 hours, switch the analyzer to sample zero air. Record the zero baseline and switch to the test gas. Verify the pollutant concentration C_{80} and record the response R_{80}.

5. Continue Steps 3 and 4 for 100 hrs or until the response at R_{80} either:

    a. exceeds the manufacturer's stated specifications for noise or drift at zero and span, or

    b. exceeds the noise or drift values obtained in Procedures 4.8, 4.9 or 4.10 or

c. the unit is no longer operational (i.e., out of supplies, analyzer stoppage, analyzer breakdown, etc.).

6. Note the time t_{uo}.

4.19.3 Calculations:

Determine the unattended operation time UO as follows:

$$UO = t_{uo} - t_o$$

TABLE 4-I

MANUFACTURER'S DATA SHEET

Date: ____________________

Test Date(s): ____________________

A. IDENTIFICATION

1. Manufacturer ____________________ Phone ____________________

   Address ____________________

2. Vendor ____________________ Phone ____________________

   Address ____________________

3. Tradename(s): ____________________ 4. Model(s): ____________________

5. Serial No(s): ____________________

6. Measurement Principle(s): ____________________

B. APPLICATION

1. Pollutant(s):

Pollutant(s)		Measuring Range ppm	

C. PHYSICAL

1. Size, Weight:

Description of Unit	Dimensions (W x H x D, cm)	Weight (kg)
Overall Size and Weight		

TABLE 4-I (Continued)

2. Space required (H x W x D, cm): ____________________________

3. Mobility: Mobile __ Portable __ Stationary __

4. Signal Output

Pollutant	Output Range	Units (volt, ma, Ω)	Linearity

D. REQUIREMENTS

1. Sampling Rate, l/min ______

2. Reagent(s):

Item	Consumption Rate (ml/min)	Storage Captacity (ℓ)

3. Utilities

Item	Consumption Rate (ℓ/min)

4. Power

Voltage (AC or DC)	Range	Current (amp, ma)	Regulation Required, %

TABLE 4-I (Continued)

5. Calibration

Dynamic ___ Static (specify method) ______________________________

E. SPECIAL FEATURES

TABLE 4-II

ANALYZER SUMMARY SHEET AND TEST RESULTS

Test Procedure	(A) Manufacturer's Specifications	(B) Test Results
4.2 Physical Description		
a. Weight (kg)	____________	____________
b. Size, W x H x D (cm)	____________	____________
c. Space Requirements W x H x D (cm)	____________	____________
4.3 Instrument Operating Instructions		
a. Supplied ?	____________	____________
b. Overall score (see Table 4-III)	____________	____________
4.5 Linearity		
a. Response (linear, concave, convex)	____________	____________
b. Maximum deviation (%FS)	____________	____________
4.6 Range(s), (ppm)		
a.	____________	
b.	____________	
c.	____________	
4.7 Accuracy (%)	____________	____________
4.8 Drift at Zero (% FS)		
a. 24 hours	____________	____________
b. Maximum	____________	____________
4.9 Drift at Span (% FS)	____________	____________
a. 24 hours	____________	____________
b. Maximum	____________	____________

TABLE 4-II (Continued)

Test Procedure	(A) Manufacturer's Specifications	(B) Test Results
4.10 Noise (% FS)		
a. at 0%		
b. at 50%		
c. at span (80%)		
4.11 Precision and Response Times-mean of 10 trials (sec, min) and CV, %		
a. Lag time (up), t_ℓ		
b. time to 95%, t_{95}		
c. time to 100%, t_{100}		
d. rise time, t_r		
e. lag time (down), $t_{-\ell}$		
f. time to -95%, t_{-95}		
g. time to -100%, t_{-100}		
h. fall time, t_f		
i. precision at 50% FS, (CV, %)		
4.12 Pulse Time, t_p (min)		
4.13 Lower Detectable Limit (ppm)		
4.14 Analyzer Deadband (% FS)		
4.15 Warm-up time (min)		
4.16 Interferences (IE, %)		
Interferents		
a. ______________		
b. ______________		
c. ______________		
d. ______________		
e. ______________		

TABLE 4-II (Continued)

Test Procedure	(A) Manufacturer's Specifications	(B) Test Results
4.17 Operating Temperature Range, OTR (^{o}C)		
4.18 Operating Voltage Range, OVR (volts)		
4.19 Unattended Operation, UO (hr)		

TABLE 4-III

INSTRUMENT OPERATING INSTRUCTIONS

	SCORE
1. Instructions supplied	_____
2. Current (up-to-date)	_____
3. Applies to instrument designated	_____
4. Includes Operation & Maintenance Section and Field Repair or Service Section	_____
5. Identification	
a. Model	_____
b. Name, address & phone of manufacturer	_____
c. Name, address & phone of representative or vendor	_____
d. Name, address & phone of nearest service center	_____
e. Form for recording serial nos., modifications, date of purchase, etc.	_____
6. Operation & Maintenance Instructions	
a. Delivery & unpacking instructions	_____
b. Assembly & installation instructions	_____
c. Electrical requirements	_____
d. Utilities requirements	_____
e. Air sample flow and pressure requirements	_____
f. Environmental requirements	_____
g. Output signal characteristics	_____
h. Start-up & operation instructions	_____
i. Calibration procedure & intervals	_____
j. Maintenance procedures & intervals	_____
k. List of recommended spare parts	_____

TABLE 4-III (Continued)

	SCORE
l. Troubleshooting	____
m. Service information	____
n. Warranty	____
7. Application	
a. Purpose & use of instrument	____
b. Measuring range(s)	____
c. Description of operating principle & flow diagram	____
d. Physical and performance specifications	____
8. Repair Instructions	
a. Physical description	____
b. Mechanical description	____
c. Electrical/electronic description	____
d. Calibration & adjustment procedures	____
e. Field repair procedures	____

____
TOTAL SCORE

Table 4 - IV

LINEARITY SUMMARY SHEET

(a)	(b)	(c)	(d)	(e)	(f)	(g)
X (input)	Y (analyzer reading)	X^2	Y^2	XY	$\hat{Y}$ (expected reading)	Deviation (b) - (f)
$\Sigma X=$	$\Sigma Y=$	$\Sigma X^2=$	$\Sigma Y^2=$	$\Sigma XY=$		

Equation of the line:

ANALYZER READING = ________ (intercept) + ________ (slope) X Input Conc

Deviation pattern ____________________ Maximum deviation ______________ %

LINEARITY:
☐ LINEAR -- maximum deviation $<4\%$ and any deviation pattern
☐ NON-LINEAR -- maximum deviation $\geqslant 4\%$, and convex or concave deviation pattern
☐ LINEAR (poor precision) -- max deviation $\geqslant 4\%$ and random deviation pattern

Table 4 - V

WORKSHEET FOR LINEAR RELATION*

X denotes (input concentration)

$\Sigma X =$ ______

Y denotes (analyzer reading)

$\Sigma Y =$ ______

Number of Points: $n =$ ______

Step (1) ΣXY = ______

(2) $(\Sigma X)(\Sigma Y)/n$ = ______

(3) $S_{xy} = (1) - (2)$ = ______

(4) $\overline{X} = \Sigma X/n$ = ______

(5) $\overline{Y} = \Sigma Y/n$ = ______

(6) ΣX^2 = ______

(7) $(\Sigma X)^2/n$ = ______

(8) $S_{xx} = (6) - (7)$ = ______

(9) $b = \frac{S_{xy}}{S_{xx}} = \frac{(3)}{(8)}$ = ______ ** (slope)

(10) $b\overline{X} = (9) \times (4) =$ ______

(11) $a = \overline{Y} - b\overline{X}$

$= (5) - (10) =$ ______ ** (intercept)

Equation of the line:

$\widehat{Y} = a + bX$

______

---

* adapted from Natrella, MG: Experimental Statistics. National Bureau of Standards Handbook No. 91 (1966)

** enter value in Table 4 - IV

TABLE 4-VI

WORKSHEET FOR RESPONSE TIMES

Trials n = 10	Times to Respond (Units____________)							
	t_1	t_{95}	t_{100}	t_r	t_{-1}	t_{-95}	t_{-100}	t_f
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
(a) Σt =								
(b) Mean = $\frac{(a)}{n}$ =								
(c) Σt^2 =								
(d) $\frac{(\Sigma t)^2}{n} = \frac{(a)^2}{n}$ =								
(e) = (c) - (d) =								
(f) = $\frac{(e)}{n-1}$ =								
(g) Std Dev = $\sqrt{(f)}$ =								
(h) CV = $\frac{(g)}{(b)}$ X 100 =								

TABLE 4-VII

WORKSHEET FOR PRECISION

(a) Input Concentration ________ ppm

Trials n = 10	Y net analyzer reading	R (c) times Y	R^2
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
TOTAL			

(b) Mean Analyzer Reading = $\frac{\Sigma Y}{n}$ = ________

(c) Conversion Factor = $\frac{(b)}{(a)}$ = ________

(d) ΣR = ________

(e) Mean Response = $\frac{(d)}{(n)}$ = ________

(f) ΣR^2 = ________

(g) $\frac{(\Sigma R)^2}{n} = \frac{(d)^2}{n}$ = ________

(h) = (f) - (g) = ________

(i) = $\frac{(h)}{n-1}$ = ________

(j) Std Dev = $\sqrt{(i)}$ = ________

(k) CV = $\frac{(j)}{(e)}$ X 100 = ________

TABLE 4-VIII

INTERFERENT TEST CONCENTRATIONS

		Interferent Concentration-ppm[a]								
Pollutant	Measuring Principle	Ammonia	Carbon Dioxide	Chlorine	Hydrogen Sulfide	Nitric Oxide	Nitrogen Dioxide	Ozone	Sulfur Dioxide	Water Vapor[c]
CO	NDIR		1000							80
CO	Mercury Replacement				0.1					80
NO_2	Colorimetric - azo dye			0.5	0.1	0.5		0.5	0.5	
NO_2	Amperometric			0.5	0.1	0.5		0.5		80
NO_2	Chemiluminescent - Gas Phase	0.5				0.5			0.5	80
O_3	Amperometric			0.5	0.1[b]	0.5[b]	0.5		0.5	80
O_3	Colorimetric - KI			0.5		0.5[b]	0.5		0.5	80
O_3	Electrochemical Concentration cell			0.5			0.5		0.5	80
O_3	Chemiluminescent - Gas Phase					0.5				80
O_3	Spectrometric									80
SO_2	Amperometric			0.5	0.1		0.5	1.0		

TABLE 4-VIII (Continued)

Pollutant	Measuring Principle	Interferent Concentration-ppm[a]								
		Ammonia	Carbon Dioxide	Chlorine	Hydrogen Sulfide	Nitric Oxide	Nitrogen Dioxide	Ozone	Sulfur Dioxide	Water Vapor[c]
SO_2	Colorimetric			0.5	0.1		0.5	1.0		
SO_2	Conductimetric	0.5		0.5	0.1		0.5	1.0		
SO_2	Flame Photometric	0.5		0.5	0.1		0.5			

a. Prepare concentrations to stated value ± 5%.

b. Do not mix with pollutant.

c. % RH.

TABLE 4-IX

PPM vs μg/m^3 Conversion Factors For Selected Gases

Desired / Given	PPM at 25°C and 760 Torr								
	NH_3	Cl_2	H_2S	NO	NO_2	O_3	SO_2	CO	CO_2
μg/m^3	1.44×10^{-3}	3.45×10^{-4}	7.18×10^{-4}	8.15×10^{-4}	5.32×10^{-4}	5.10×10^{-4}	3.82×10^{-4}	-	-
mg/m^3	-	-	-	-	-	-	-	0.874	0.556

Desired / Given	μg/m^3							mg/m^3	
	NH_3	Cl_2	H_2S	NO	NO_2	O_3	SO_2	CO	CO_2
PPM	696	2900	1390	1230	1880	1960	2620	1.14	1.80

Multiply the given value by the factor under the appropriate gas to obtain the desired unit.

5.0 GAS GENERATION

5.1 PRINCIPLES AND SCOPE

To conduct the analyzer performance tests described in Chapter 4 requires the availability of stable test atmospheres which contain known concentrations of pollutant and interferent gases for extended periods (days). In general, a test atmosphere is produced by mixing a flow of the desired test gas with flows of clean, dry air (zero air). The test gas may be obtained by dilution of a concentrated gas from a permeation device or a cylinder, further dilution of a dilute gas, or generated from another medium as in the case of oxygen photolysis to produce ozone. The dilutions are prepared in a gas mixing apparatus prior to entering a delivery manifold. This manifold is designed to accommodate simultaneously the sample probe of the analyzer and the independent referee method (Figure 5-I).

This chapter provides instructions for generating the various pollutant and interferent test gases that are needed. In using these instructions, previous experience and training in gas dynamics and trace gas analysis are helpful.

5.1.1 Range

The concentration and volume of the test gases required depend on the measuring range and the sampling rates of the analyzer(s) to be tested and the range of the referee method.

Typical analyzer measuring ranges and sampling rates are summarized in Table 5-I. The concentrations range from 0.01 to 100 ppm and sampling rates vary from 0.1 to 5.0 l/min.

5.1.2 Interferences

Pure pollutant and interferent gases can be purchased with a purity of 99% or better. Selective absorbers can be used to remove further unwanted trace substances. Descriptions of absorbers that have been found useful are given in Table 5-III. See 5.2.2 for zero air specifications.

5.1.3 Precision

The precision (coefficient of variation) with which the test gas concentrations can be prepared depends on 1) the nature of the test gas and 2) the precision of the method used to establish the concentration. With careful work, a precision between 2 to 5% is achievable[1] in the preparation of gases such as CO, SO_2 and NO_2. A portion of the error is in the determination of air volumes stemming from the use of rotameters. A minimum of 2% error is produced for each rotameter and the errors are usually additive. Pulsating flows and pressure differences in the gas generation systems produce some flow variation which also tends to decrease precision.

Another source of error is the precision of the referee procedure; there is little information in this regard. When the referee method is a colorimetric procedure, the limiting factors are often in the measurement of the sample air volume and the absorbance of the colored reagent.

5.2 APPARATUS

This section specifies the equipment components and materials needed for generating and verifying the test gas concentrations.

The gas generating system consists of a) sources of the pollutant and interferent gases (permeation system, cylinder of gas, ozone generator, etc.), b) source of zero air, c) a gas mixing apparatus, d) a delivery manifold and e) provisions for collecting samples for independent analysis. The individual gas flows - zero air, pollutant and interferent - are homogenized and delivered to the test analyzer(s).

The procedures for generating the test gases are summarized in Table 5-II along with the referee methods for the verification or establishment of the test gas concentrations. Additional information and discussion concerning the theoretical and practical aspects of gas generation can be obtained in "Controlled Test Atmospheres" by G. O. Nelson[2].

Any gas generation system should meet the following general specifications:

1. Produce the required pollutant and interferent gases.

2. Generate gas concentrations to cover the measuring ranges of the analyzers to be tested.

3. Provide sufficient gas flow to accommodate the sampling requirements.

4. Maintain stable output for the required test duration.

5. Simulate rapid (seconds) step changes in gas concentration.

6. Generate multicomponent gas mixtures.

7. Deliver flows of zero air and the test gas simultaneously through separate ducts.

8. Maintain the difference in pressure at the point of delivery to ± 0.5 inch H_2O (0.012 Newton/cm^2) of atmospheric.

9. Utilize ducts, valves, rotameter, mixing chambers etc. with surfaces that will not alter the test gas composition.

Mount the components on a chassis for convenience.

5.2.1 Gas Mixing Apparatus

The gas mixing apparatus consists of an array of flowmeters, metering valves, a glass mixing chamber and delivery manifold as shown in Figure 5-I.

1. Flowmeters: Calibrated flowmeters are needed to measure a) a flow of zero air equal to the sum of the flow required by the test analyzers, the referee procedure and 10% excess, and b) the range of gas flows required to produce the pollutant and interferent test concentrations. Glass rotameters are commonly used. Calibrate all rotameters in the system with a primary or secondary standard such as a soap bubble meter, frictionless piston, wet-test meter, spirometer or dry gas meter.

2. Mixing Chamber: This is a vessel with inlet and outlet ports for mixing the individual test gases. The configurations of some typical mixing chambers are shown in Figure 5-II. Design A is the simplest and is usually adequate. Design B permits the addition and mixing of several gases simultaneously. When chambers of other configurations are used, make sure they accommodate the required gas volumes and flows and provide homogeneous mixtures[2].

3. Delivery Manifold: This consists of a borosilicate glass duct with several ports for sampling the test gas mixture simultaneously with the test analyzer(s) and the referee procedure. The inside diameter of the duct and ports should be sufficiently large so that the pressure and flow conditions within the analyzer will not be altered by more than 2% during sampling.

4. Metering Valves: Fine control needle valves should be stainless steel or Teflon for pollutant and interferent gases and any material for zero air.

5.2.2 Zero Air Production

The zero air for diluting the test gases should be free of any substances that will in any way a) alter the test analyzer response, b) react with the pollutant or the interferent and c) interfere in the referee procedure. (NOTE: It is not necessary to remove substances that are known not to interfere in the test analyzers and referee measurement methods.) The zero air may be supplied from cylinders or by filtering of ambient air.

1. Cylinder Zero Air[3,10]: Cylinders should be fitted with a two-stage pressure regulator and a metering valve. For uninterupted operation, several cylinders may be connected to the same line. While it

is possible to prepare zero air in cylinders in the laboratory, this requires access to a high pressure (1,000 to 2,000 psig) air compressor.

2. Filtered Zero Air: For diluent flow requirements $\leq$ 7 l/min, zero air can be prepared by passing ambient air through a commercial breathing mask filter[4] designed for removing acid gases and organic vapors. This filter, installed in a special holder[5], removes NO_2, SO_2, O_3, most other acid and organic gases and vapors and partially removes NO. It does not remove CO or CO_2.

   To remove substances not eliminated by this filter and to purify larger air volumes (up to 30 l/min.) the ambient air is passed through a series of chemical filters designed to remove specific constituents. The filter materials required, the purpose of each and the method of preparation are summarized in Table 5-III. To trap particulate matter that might be released into the air stream, install a glass fiber mat particle filter just prior to discharging the zero air.

3. Air Pump (for transport of ambient air): Vane, piston or diaphragm air pumps are used to furnish the diluent air flow required for the gas mixing apparatus. Diaphragm-type pumps are recommended since carbon ring and carbon vane-type pumps may

release particulate matter into the air stream. Oil lubricated pumps should not be used. A particle filter is necessary for vane pumps and is optional with diaphragm types. Diaphragm and piston pumps often deliver pulsating flows. To minimize or eliminate such variations, install an expansion tank in the pump discharge line.

5.2.3 Gas Permeation Apparatus (Figure 5-III)

Using permeation devices as sources for gases require a constant temperature bath, a temperature conditioning coil and a permeation device holder.

1. Constant Temperature Bath: A bath in the range of 20 to 30°C and controlled to ± 0.1°C is needed.

2. Temperature Conditioning Coil: A coil of metal tubing is used for equilibrating the temperature of the carrier gas. A section of copper tube 1/4 to 3/8 in. ID (0.64 to 0.95 cm) by 25 to 50 ft (76 to 152 m) long is usually adequate.

3. Thermometer: Use a laboratory type thermometer suitable for measuring between 20 to 30°C with an accuracy of 0.1°C.

4. Permeation Device Holder: The holder is made from a borosilicate glass screw-cap test tube with added inlet and outlet ports (Figure 5-IV). All connections must be water-tight.

5. Permeation Device: This is a source for some of the test gases listed in Table 5-II. The devices may be purchased[6,7] or prepared in the laboratory[8,9].

5.2.4 Compressed Cylinder Gases

High pressure cylinders containing dilute concentrations of test gases such as carbon monoxide (CO), carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) can be purchased[3,10] or prepared in the laboratory. The concentrations should be at least twice and preferably 10 to 100 times the desired test concentration. The maximum useful cylinder concentration is determined by the gas volumes and rates that can be reasonably handled by the gas mixing system.

A cylinder of gas is prepared in the laboratory by transferring the appropriate volume of the pure test gas to an evacuated cylinder. The cylinder is then pressurized with the desired diluent gas. The transfer is made with a closed system vacuum-pressure manifold[11]. Care must be taken to avoid contamination of the pure gas with air and water vapor or accidental release of the toxic gas into the work environment.

The losses of some test gases are minimized by using stainless steel containers or containers coated with a non-reactive lining such as chromium molybdenum alloy, paraffin or Teflon, or containers with "conditioned" surfaces. Conditioning involves repeating filling and emptying of the container with the test gas until referee analysis shows no further changes in concentration occur with time. In any event, a container previously filled with a particular test gas should be refilled only with the same test gas and concentration. In an emergency, cylinders known to have contained gases such as air or nitrogen may be refilled with a different gas.

Cylinder gases should be analyzed before each use. CO concentrations should be verified monthly by independent analysis for the first six months after purchase or preparation and about every 6 months thereafter. Certification or analysis by the supplier at the time of preparation is often of little value because changes have frequently been observed. When cylinder pressures deplete to 200 to 500 psig; (138 to 345 Newton/cm^2) the concentrations of some gases increase due to wall desorption. The gases should be analyzed more frequently or preferably the cylinders should be refilled. After equilibration and confirmation or verification of the concentrations by referee analysis, the gases are ready for use. In the case of some gases, notably NO_2, it may be necessary before use to bleed the cylinders at 30 to 50 ml/min for up to two hours to condition the delivery lines.

5.2.5 Ozone Generation

Several commercial ozone generators have recently become available. An adequate generator can also be assembled in the laboratory with readily available components. See Figure 5-V and 6.5.1 in Chapter 6 for the list of equipment. NOTE: The generator in Figure 5-V uses a larger lamp and chamber than in Figure 6-II to furnish larger gas volumes for testing several analyzers simultaneously.

Ozone up to 2 ppm is produced by irradiating a stream of zero air to ultra-violet light from a mercury vapor lamp. A portion of the oxygen in the air is converted to ozone. The air may be passed through a chamber in which the lamp is inserted or the lamp may be located outside the chamber as in Figure 5-V. In this latter design, the chamber should be of quartz to allow the radiation to pass through. Depending on the generator design, changes in concentration are obtained by a) the adjustment of a movable shade over the lamp which controls the amount of radiation, b) varying the airflow through the chamber, c) adjusting the lamp voltage or d) dilution of the ozonized air with zero air. In some designs, the distance between the lamp and chamber can be varied. The concentrations can be further increased by using oxygen in place of air.

Although ozone can be obtained dissolved in liquid chlorotrifluoromethane (Freon 13)[3], it is not recommended because of a) cost, b) limited durability (days), c) toxicity and d) possibility of explosion at temperatures above -20°C[12].

5.2.6 Humidity Generator

The generator consists of a glass vessel (humidifier) containing distilled water and a moisture sensor. Humidified air is produced by passing zero air over the distilled water in the humidifier maintained at a fixed temperature between 20 to 30°C so that a relative humidity between 70 to 80% is produced.

1. Humidifier: This can be a 250 or 500 ml Erlenmeyer or equivalent flask with an inlet tube extending to within 1 to 2 cm above the water level.

2. Moisture Sensor: A commercially available moisture sensor such as a LiCl salt type sensor, dew-point detector or continuous wet and dry bulb recorder may be used.

5.2.7 Sampling and Analysis

The referee procedure generally is a manual method and requires a sampling train consisting of sampling probes, absorbers, metering valves, flowmeters, vacuum pumps and traps as shown in Figures 6-III, 7-II and 8-II.

1. Sampling Probes: All sampling lines for the referee procedure should be of glass or Teflon, and should be as short as possible to prevent transit losses. Short sections of polyvinylchloride tubing (like Tygon) may be used for butt-joints only.

2. Absorbers: All-glass bubblers or midget impingers are described in the respective referee procedures. The absorbers may be purchased from major glassware suppliers. For some tests, two absorbers in series may be needed to insure complete collection of the air sample. Standard ball-joints are commonly used to facilitate on-off connections.

3. Air-Vacuum Pump: This is needed to draw up to 2.0 liters/min through the absorbers. The pump should be equipped with a trap and a needle valve at the inlet side to regulate flow.

4. Thermometer: An accuracy of ± 2°C is needed to correct the sampled gas volumes to standard conditions (25°C, 760 torr).

5. Metering Valve: A fine control needle valve is used to regulate sample flow.

6. Barometer: This is used to correct the sample gas volumes to standard conditions and should be accurate to the nearest torr.

7. Flowmeter: A calibrated rotameter to measure gas flows between 0.5 to 3 liters/min within ± 2%.

8. Trap: A vessel which contains glass wool to protect the needle valve and the vacuum pump from moisture.

9. Spectrophotometer: This is used to measure the absorbance of solutions between 350 to 600 nm. The references listed in Table 5-II cite bandpass requirements.

10. Other: Chemicals, reagents and other apparatus needed to perform the referee analysis are specified in the references listed in Table 5-II.

5.3 OPERATION OF THE SYSTEM

The test gases and the concentrations needed and the instructions for generating them are described under the respective tests in Chapter 4. Information regarding the criteria of components for the gas generating systems and additional details concerning other methods and equipment for generating test atmospheres are found in Reference 2.

5.4 REFERENCES

1. Thomas MA, and Amtower RE: Gas dilution apparatus for reproducible dynamic gas mixtures in any desired concentration and complexity. J Air Poll Cont Assn, 16-618, 1966

2. Nelson GO: Controlled Test Atmospheres. Ann Arbor Science Publisher, Inc. (1971)

3. Matheson Gas Products, 61 Grove Street, Gloucester, MA 01930

4. Filter Cartridge, (GMC fill), Cat. No. DZ-78006, Mine Safety Appliances, 201 North Braddock Avenue, Pittsburgh, PA 15028

5. Filter Holder, End of Line, Cat. No. DZ-78006, Ibid

6. Analytical Instrument Development, Inc., 250 South Franklin Street, West Chester, PA 19380

7. Metronics Associates, Inc., 3201 Porter Drive, Stanford Industrial Park, Palo Alto, CA 94304

8. O'Keeffe AE , Ortman GC: Primary standards for trace gas analysis. Anal Chem 38, 760 (1966)

9. Scaringelli FP, O'Keeffe AE, Rosenberg E, Bell JP: Preparation of known concentrations of gases and vapors with permeation devices calibrated gravimetrically. Anal Chem 42, 871 (1970)

10. Scott Research Laboratories, Inc., Plumsteadville, PA

11. Belsky T: Preparation of low-concentration mixtures of gases. Air and Industrial Hygiene Lab, Cal State Dept of Publ Hlth, Berkeley, CA 94704, AIHL Report No. 117 (Jan. 1972)

12. Braker W, Mossman AL: Effects of exposure to toxic gases. Matheson Gas Products, Div Will Ross Co, NJ (July 20, 1970)

TABLE 5-I

MEASURING RANGES AND SAMPLING RATES OF COMMON AIR ANALYZERS

POLLUTANT	MEASUREMENT PRINCIPLE	MEASURING RANGE (Upper Limit) ppm	SAMPLING RATE 1/min
CO	NDIR	25 to 100	0.5 to 2.0
	Hg replacement	5 to 50	8 to 41[a]
O_3	Amperometric	0.1 to 2	0.15 to 4.0
	Chemiluminescent	0.02 to 2	1.0 to 2.0
	Colorimetric	0.5 to 5	0.25 to 4.0
	Electrochemical Cell	0.025 to 1	0.10
	UV Absorption	0.5 to 2	3.0
NO/NO_2	Amperometric	0.1 to 2	0.15 to 3.5
	Chemiluminescent	0.1 to 2	
	Colorimetric	0.1 to 2	0.2 to 3.5
SO_2	Amperometric	0.1 to 2	0.15 to 3.5
	Colorimetric	0.25 to 5	0.4 to 1.0
	Conductimetric	0.5 to 2	0.1 to 5
	Flame Photometric	0.01 to 1	0.15
	Electrochemical Transducer	1 to 5	0.2 to 0.5

[a] Rate of interferent prefilter section. Detector section samples at 1 to 2 liter/min.

TABLE 5-II

METHODS FOR GENERATING AND DETERMINING GAS CONCENTRATIONS

TEST GAS	GENERATION	REFEREE METHOD
1. Ammonia	Permeation tube and procedure described for SO_2 in footnote 3.	Tentative Method of Analysis for Ammonia in the Atmosphere (Indophenol Method). 42604-01-72T, footnote 1.
2. Carbon Dioxide	A cylinder of zero air containing 10,000 ppm CO_2. Dilute with zero air to concentration specified in Table 4-VIII.	Certified analysis by manufacturer, vendor or independent laboratory.
3. Carbon Monoxide	A cylinder of zero air containing CO concentrations 10 to 100 times those required in the test procedure. Dilute with zero air to concentration needed.	Certified analysis by manufacturer, vendor or independent laboratory.
4. Chlorine	Permeation tube and procedure described for SO_2 in footnote 3.	Tentative Method of Analysis for Free Chlorine Content of the Atmosphere (Methyl Orange Method). 42215-01-70T, pg 282, footnote 2.
5. Hydrogen Sulfide	Permeation tube and procedure similar to that described for SO_2 in footnote 3.	Tentative Method of Analysis for Hydrogen Sulfide Content of the Atmosphere, 42402-01-70T, pg 426, footnote 2.
6. Nitric Oxide	Cylinder of nitrogen containing 20 ppm NO and less than 4 ppm O_2. Dilute with zero air to desired concentration.	Tentative Method of Analysis for Nitric Oxide Content of the Atmosphere (Greiss-Saltzman Reaction), 42601-01-71T, pg 325, footnote 2.
7. Nitrogen Dioxide	Cylinder of nitrogen containing 20 ppm NO_2. Dilute with zero air to desired concentration. (NOTE: To condition regulator and delivery lines, discharge the NO_2 at a low (~ 30 ml/min) rate until the concentration is stable (usually within one hour).	Tentative Method of Analysis for Nitrogen Dioxide Content of the Atmosphere (Greiss-Saltzman Reaction), 42602-01-68T, pg 329, footnote 2.

TABLE 5-II (Cont'd)

TEST GAS	GENERATION	REFEREE METHOD
7. Nitrogen Dioxide (Cont'd)	Permeation tube and procedure described for SO_2 in footnote 3. Air in contact with permeation tube must have a RH $< 5\%$. Tube should be weighed weekly.	Ibid (preferred) or emission rate certified by manufacturer, or by independent laboratory.
8. Ozone	Ozone generator - procedure described in footnote 3.	Tentative Method of Analysis for Oxidizing Substances in the Atmosphere, 44101-01-70T, pg 351, footnote 2.
9. Sulfur Dioxide	Permeation tube and procedure described in reference method for SO_2, footnote 3.	Pararosaniline procedure described in footnote 3.
10. Water	Pass zero air over water at a fixed temperature between 20 to 30°C to obtain 80 to 90% RH. Dilute with zero air to desired RH.	Dewpoint detector, calibrated hygrometer or a wet/dry bulb thermometer.
11. Zero Air	Air containing 21.0 ± 0.5% oxygen and no constituents that will 1) react with the pollutant or interferent gas 2) alter the test analyzer response and 3) interfere in the referee procedure.	Cylinder zero air: certified analysis by manufacturer or vendor. Filtered zero air: compare response of referee method and test analyzer(s) with response obtained with certified cylinder zero air.

1 Health Lab Sciences, 10:2, 115-118, Apr 1973.

2 Manual of Methods of Ambient Air Sampling and Analysis. Intersociety Committee, 1972. Amer. Public Health Assn., 1015 - 18th Street N.W., Washington, DC.

3 Part 50 - National Primary and Secondary Ambient Air Quality Standards, Federal Register, Nov. 25, 1972 (26 FR 22384)

TABLE 5-III

ABSORBERS FOR PRODUCING ZERO AIR UP TO 30 1/min

MATERIAL	PURPOSE	PREPARATION
1. Activated charcoal (6 x 16 mesh)	Removes many gases such as ozone, SO_2, NO_2, higher molecular weight organic vapors. Does not remove CO, CO_2.	Commercially activated coconut hull charcoal 6 x 16 mesh[1]. Place in 2 inch I.D. x 18 inch long section of plastic pipe. Use glass wool plugs to retain charcoal in place. Plastic pipe caps on each end of cylinder are drilled and threaded to accept standard 1/2 inch O.D. tube fittings. Containers of other materials and similar configuration and volume may be used.
2. NO Oxidizer		
(a) Chromium trioxide (CrO_3)	Converts NO to NO_2 for subsequent removal with TEA or soda lime[4].	Soak firebrick or alumina 15-40 mesh in a solution containing 16 g CrO_3 in 100 ml of water. Drain, dry in an oven at 105-115°C for 30 to 60 minutes and cool. Spread a thin layer of the dry pellets in a dish and place in a desiccator containing a saturated salt solution which maintains the relative humidity between 50 to 70%. The reddish color changes to a golden orange when equilibrated. Place in a 1/2 inch I.D. x 15 inch glass tube. Use glass wool plugs to hold pellets in place. (Caution: Protect eyes and skin when handling this material. Do not breathe oxidizer dust.) Before using, pass air containing 30 to 70% RH through the oxidizer for about 1 hour at 0.5 ℓ/min to condition. Discard when more than 3/4 of the oxidizer bed depth turns brown.
(b) Humidifier	Furnishes water vapor for proper operation of oxidizer.	Pass dilute NO air stream over water at a fixed temperature such that the humidity of the air stream is maintained within 50 ± 20% R.H.

TABLE 5-III (Cont'd)

MATERIAL	PURPOSE	PREPARATION
3. Triethanolamine (TEA)	Removes NO_2	Soak firebrick 10-20 mesh in a 20% aqueous solution of TEA. Drain, spread on a dish. and dry for 30 to 60 min at 95°C. Pellets should be free-flowing. Place in a 1/2 inch O.D. (7/16 inch I.D.) x 15 inch long polyethylene or stainless steel tube with standard 1/2 inch O.D. tube fittings on each end. Use glass wool plugs to hold the pellets in place.
4. Desiccant	Remove water	Commercial 6 x 16 mesh silica gel with color indicator[2]. Place in 3 inch I.D. x 24 inch long clear plastic cylinder capped at both ends. Caps are drilled and threaded to accommodate standard 1/2 inch O.D. tube fittings. Use glass wool to hold granules in place. When the change in color exceeds 3/4 of the desiccant bed depth, regenerate by exposing the silica gel to 120°C atmosphere overnight.
5. Carbon Monoxide Oxidizer (Hopcalite)	Catalytically oxidize CO to CO_2 for subsequent removal with Ascarite or soda lime.	Commercial mixture of copper and manganese oxides[3]. Place granules in a 1/2 inch O.D. (7/16 inch I.D.) x 15 inch long section of copper pipe with standard 1/2 inch O.D. tube fittings on each end. Use glass wool to hold granules in place.
6. CO_2 Absorber	Remove CO_2, H_2O	a. Soda Lime[4]: commercial mixture of calcium and sodium hydroxides; 4 to 8 mesh. b. Ascarite[5] : a commercial preparation of sodium hydroxide in an asbestos matrix, 8-30 mesh.

TABLE 5-III (Cont'd)

MATERIAL	PURPOSE	PREPARATION
		Place soda lime or ascarite in a 2 inch I.D. x 15 inch long section of plastic pipe. Plastic caps at both ends are drilled and threaded to accept standard 1/2 inch O.D. tube fittings.

1 Activated coconut hull charcoal, Type PCB 6 x 16 mesh, Pittsburgh Activated Charcoal, Merk & Co., Inc. Pittsburgh, PA 15230

2 Silica gel, indicating, 6 x 16 mesh, Grace Davison Chemical, Baltimore, MD 21226

3 Carbon monoxide purifier, (Hopcalite) Model RAF-BCHDI, Robbins Aviation, Inc., Vernon, CA 90058

4 Soda lime, 4-8 mesh, J.T. Baker Chemical Co., Phillipsburg, NJ 08865

5 Ascarite, 8-30 mesh, ibid.

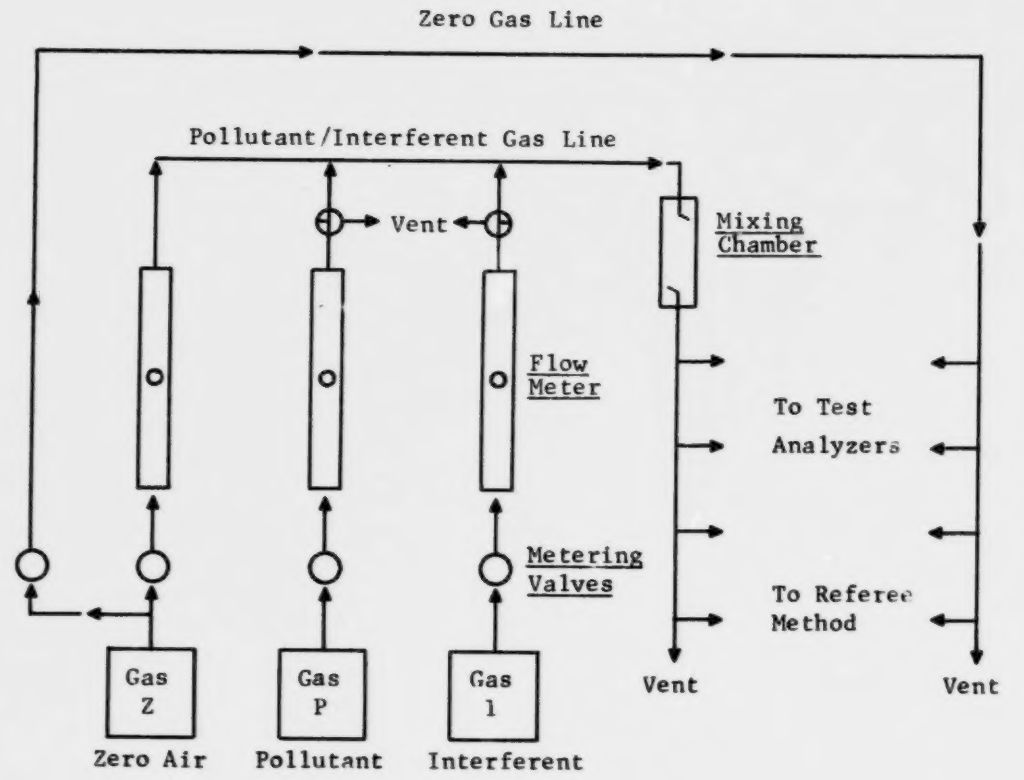

Zero Gas Line
Pollutant/Interferent Gas Line
Vent
Mixing Chamber
Flow Meter
Metering Valves
To Test Analyzers
To Referee Method
Vent
Vent
Gas Z
Gas P
Gas 1
Zero Air
Pollutant
Interferent

Figure 5-I. Diagram of gas mixing apparatus

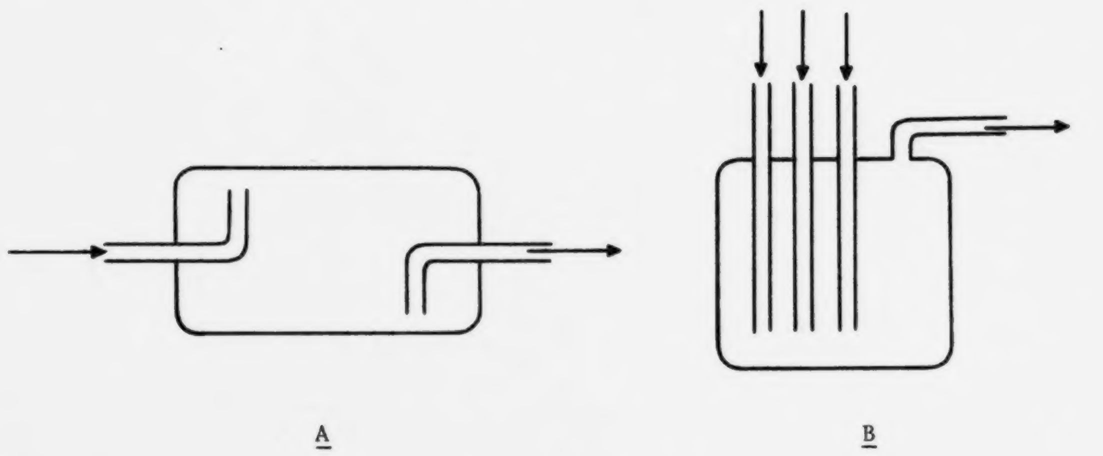


Figure 5-II. Configuration of gas mixing chambers.

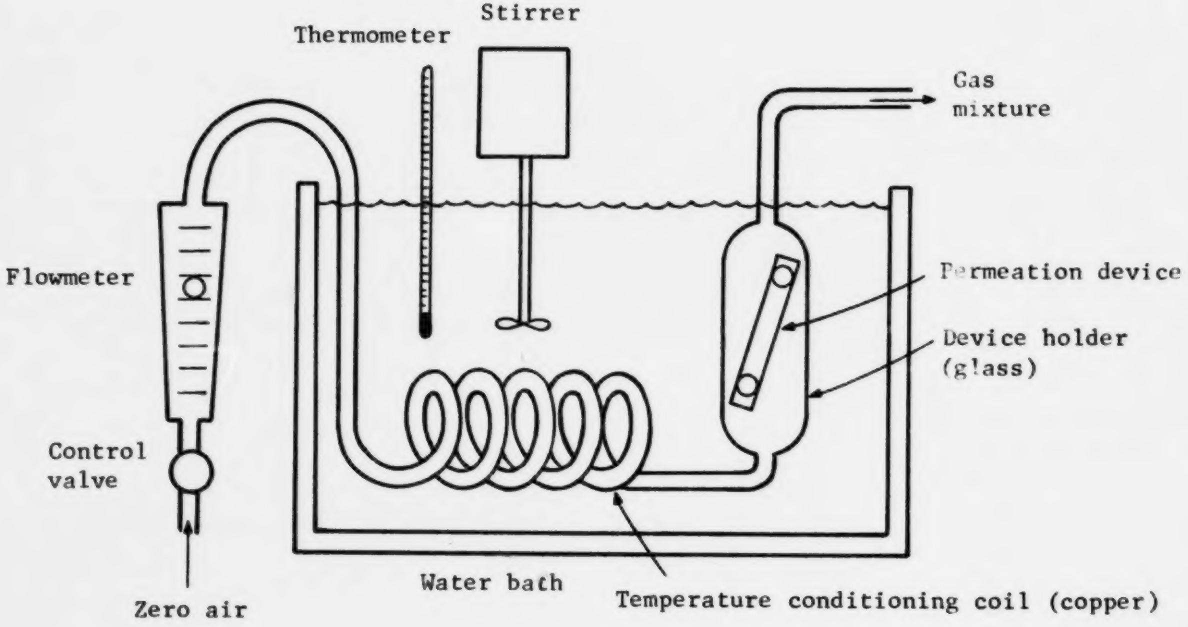
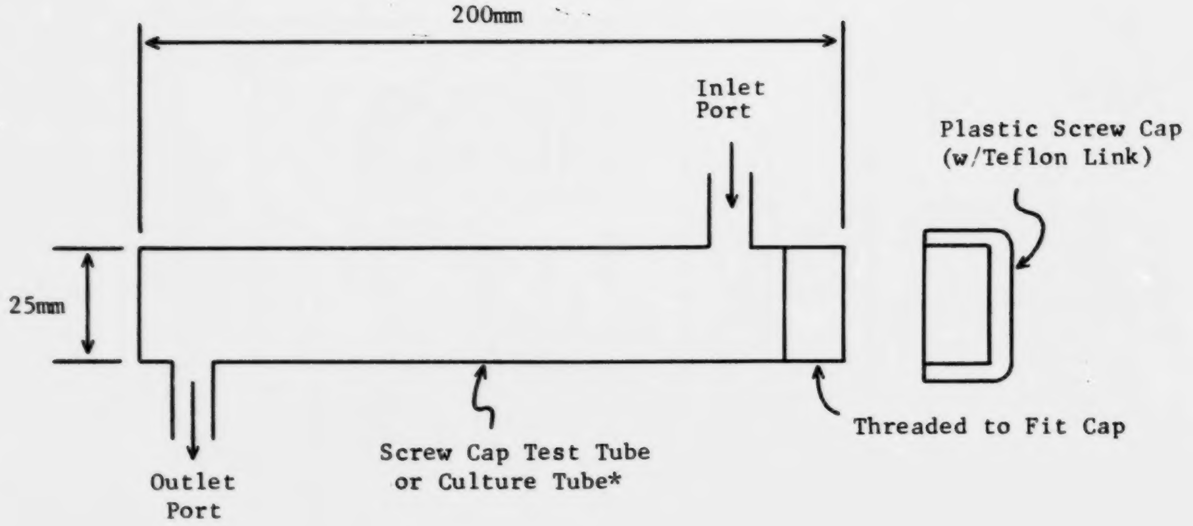

Thermometer
Stirrer
Gas
mixture
Flowmeter
Permeation device
Device holder
(glass)
Control
valve
Zero air
Water bath
Temperature conditioning coil (copper)

Figure 5-III. Gas permeation apparatus.


200mm
Inlet
Port
Plastic Screw Cap
(w/Teflon Link)
25mm
Threaded to Fit Cap
Outlet
Port
Screw Cap Test Tube
or Culture Tube*

* Kimble Glass Co., Div. Owens-Illinois, Toledo, Ohio. Cat. No. 45066.

Figure 5-IV. Permeation device holder.

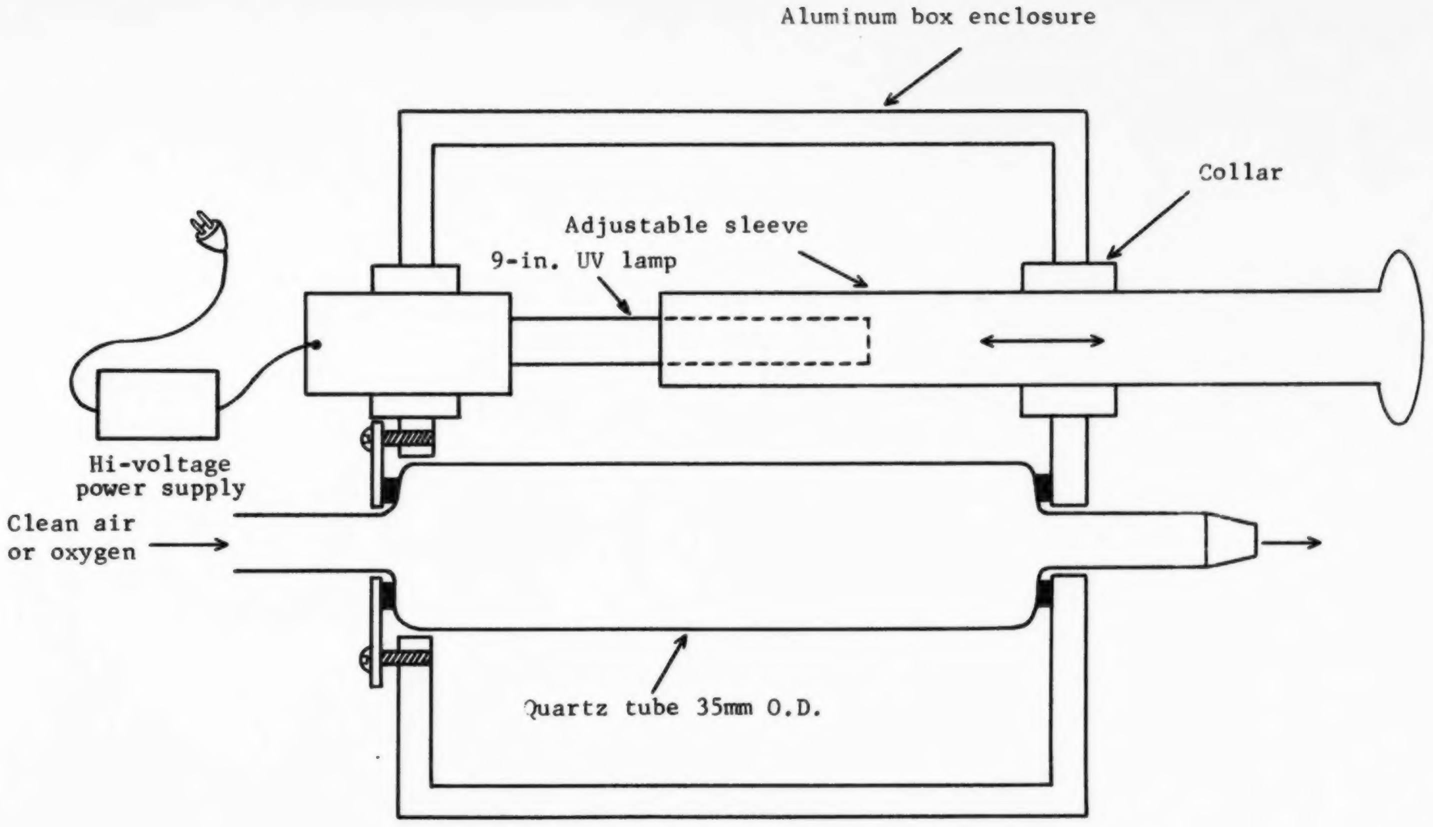

Aluminum box enclosure
Collar
Adjustable sleeve
9-in. UV lamp
Hi-voltage
power supply
Clean air
or oxygen
Quartz tube 35mm O.D.

Figure 5-V. Ozone Generator

6.0 CALIBRATION PROCEDURE FOR AUTOMATED ATMOSPHERIC OXIDANT AND OZONE ANALYZERS

6.1 PRINCIPLE AND SCOPE

6.1.1 This procedure is for the calibration of automated atmospheric oxidants and ozone analyzers. The calibration may be of two types, dynamic and static. The dynamic calibration must always be performed by determining the analyzer response to a series of ozone (O_3) concentrations. The procedure is applicable to all oxidant and ozone analyzers and is a performance test of the entire analyzer under simulated service conditions. The static calibration is performed by determining the analyzer response to artificial stimuli such as standard calibrating solutions, optical filters, screens, electrical signals, resistors, etc. This calibration is a test of the detection and signal presentation components only and is not a substitute for the dynamic calibration. It is primarily applicable to analyzers using wet-chemistry and colorimetry.

6.1.2 Atmospheric oxidants are those airborne compounds that will oxidize iodide ions in solution to iodine. The predominant oxidant is ozone. Other oxidants are: nitrogen dioxide, halogens, peroxy compounds, hydroperoxides, organic nitrites, peroxy nitrates, and hydrogen peroxide. Sulfur dioxide reduces the iodine in solution. Oxidant data should be corrected for the effect of nitrogen dioxide and sulfur dioxide.

6.1.3 The ozone concentrations for the dynamic calibration are generated by irradiating a stream of purified air (or oxygen) with ultraviolet light. Each ozone stream is sampled simultaneously with the instrument and with the manual referee method (neutral potassium iodide[1]) to establish the concentration.

6.1.4 Static calibration is accomplished by flowing reagent solutions containing amounts of iodine (I_2) equivalent to concentrations of ozone through the analyzer's detector at the reagent flow conditions encountered during normal operation. The analyzer responses are plotted versus equivalent ozone concentrations to obtain the static calibration curve. The instrument variables, e.g., air and liquid flow rates, may be adjusted after static calibration to make the output response conform to the pollutant concentration or a simple multiple or fraction of the concentration in parts per million (ppm) or micrograms per cubic meter ($\mu g/m^3$) (spanning). When a static calibration is not performed, the spanning may be done during the dynamic calibration.

6.2 RANGE

The range of the calibration procedure is determined by that of the manual referee method. For a 100 liter sample collected in 10 ml of absorbing reagent and measured in a 0.5 inch cuvette, the range is between 0.02 to 1.0 ppm O_3 (40 to 2,000 μg O_3/m^3). The lower limit can be extended down to about 0.01 ppm (20 $\mu g/m^3$) by using a one inch path cuvette and a 30 minute sampling period. At concentrations below 0.05 ppm (100 $\mu g/m^3$) the manual method may be less accurate because of the losses of iodine on the glass surface[2]. The upper limit can be extended up to 10 ppm O_3 (20,000 $\mu g\ O_3/m^3$) by using 20 ml of absorbing reagent and decreasing the sampling rate and collection period.

6.3 INTERFERENCES

6.3.1 The zero air used for ozone generation must be free of reducing and oxidizing substances. Commercial zero air in cylinders is usually free of such interferents. Chemical absorbers are available that will remove most interfering compounds when ambient air is used for zero air. Details for preparing these absorbers are given in Table 5-III.

6.3.2 Glassware should be cleaned with chromic acid solution since dust or foreign matter may interfere. Rinse thoroughly with distilled water. Vessels to contain a dilute iodine solution should be rinsed just before use with a portion of the solution to avoid losses of iodine[2].

6.4 PRECISION, ACCURACY AND STABILITY

6.4.1 The coefficient of variation of the manual referee method within the range of 0 to 2 ppm is about ± 5%. The major error is from the loss of iodine. This is reduced by using a second impinger in tandem.

6.4.2 When spanning is possible, any discrepancy between the input and output may be resolved by adjusting the output of the instrument to correspond with the value of the calibrating gas or solution. Where analyzers have no spanning controls, a correction factor may be calculated to convert the analyzer readings to ozone concentrations.

The calibration is based on the 1:1 stoichiometry of the reaction of ozone in the absorbing solution[3,4,5].

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \qquad (1)$$

6.4.3 The absorbance of the reacted KI solutions in the referee procedure should be read between 15 to 30 minutes after sampling to insure complete I_2 formation and yet avoid fading of iodine color, especially at low absorbance levels.

6.5 APPARATUS

6.5.1 Ozone Generator (Figure 6-I and 6-II) The generator should be capable of producing ozone concentrations in the range of 0.01 to 1.0 ppm (20 to 200 $\mu g/m^3$) at a flow rate of at least 5 l/min.

Commercial ozone generators have recently become available. The ozone concentration produced varies inversely with the airflow rate, and directly with the exposed area of the ultraviolet lamp.

An adequate generator consists of:

1. Ultraviolet Source - Low-pressure mercury lamp such as Ultraviolet Products, Inc., San Gabriel, California, model PCQ9G-1 or equivalent (available in lengths from 6.3 to 20 cm or 2-1/2 to 8 inches), with matching power supply (ballast transformer).

2. Lamp Control - The lamp ballast should be connected to a source of constant AC voltage to provide a constant lamp output.

3. Lamp Housing - Figure 6-II shows a recommended system for exposing the air stream to the ultraviolet lamp.

4. Pump (for transport of ambient air) - capable of furnishing the total airflow requirements of the calibration system plus 10%. Diaphragm-type pumps are recommended since pumps with carbon vanes and rings may release particulate matter into the air stream. A particle filter (glass fiber mat) should be installed downstream of carbon vane pumps and is optional with diaphragm pumps.

5. Activated Charcoal Trap - For filtering cylinder air. See Table 5-III, Item 1.

6. Flowmeter - For measuring airflow past the lamp; meter should be capable of measuring flows from 1 to 10 liters/min within ± 5%. Rotameters are most commonly used. They should be calibrated frequently (at least monthly) with an appropriate flow measuring device such as a wet test meter, dry gas meter, soap bubble meter or calibrated rotameter.

7. Sampling Manifold - The manifold is fabricated from borosilicate glass tube with sampling ports to distribute the calibrating gas simultaneously to the analyzer(s) and the manual sampling train. See Figure 6-I.

6.5.2 pH meter - Capable of measuring with a precision of ± 0.02 pH units.

6.5.3 Sampling Probes - The gas lines for conducting the ozone calibrating mixtures to the analyzer should be of Teflon or glass, and they should be as short as possible to minimize wall losses. Short sections of polyvinylchloride tubing may be used to buttjoin sections of inert tubing.

6.5.4 Manual Sampling Train:

Assemble the ozone sampling train as shown in Figure 6-III. Use ground-glass joints upstream from the impingers. Other connections may be butt-joined with polyvinylchloride tubing.

1. Absorber - All-glass midget impingers as shown in Figure 6-III are recommended for collecting the samples for referee analysis. See Reference 1 for specifications. The impingers may be purchased from glassware suppliers. Two absorbers in series are needed to insure complete collection of the sample. Ball-joint connections are recommended for convenience.

2. Air-vacuum Pump - Capable of drawing 1 liter/min through the absorbers. The pump should be equipped with a needle valve and trap at the inlet side to regulate flow.

3. Flowmeter - A calibrated metering device to measure gas flows of 0.5 to 2 liters/min within ± 2%. See Item 6 in 6.5.1 for calibration requirements.

4. Trap - A vessel containing glass wool to protect needle valve from moisture.

6.5.5 Miscellaneous

1. Spectrophotometer - Equipped with a bandpass filter of 20 nm or less for measuring the absorbance at 352 nm. Matched 1-cm, 0.5 or 1.0 inch cuvettes should be used.

2. Timer - 0 to 30.0 minutes - for measuring the sampling period of the referee sample.

3. Thermometer - With an accuracy of ± 2°C to correct sample volumes to standard conditions (25°C, 760 torr).

4. Barometer - Accurate to the nearest torr to correct sample volumes to standard conditions.

6.5.6 Static Calibration

1. Volumetric Flasks - 25, 100, 250, 500, 1000 ml - low actinic glass.

2. Buret - 50 ml.

3. Pipets - 0.5, 1, 2, 3, 4, 10, 25, and 50 ml volumetric.

4. Separatory Funnel - 125 ml, low actinic glass.

5. Iodine Flasks - 300 ml., (3).

6. Oven - maintained at 105°C.

6.6 REAGENTS AND GASES

Purity of chemicals - Unless otherwise indicated, all reagent specifications shall conform to the Committee on Analytical Reagents of the

American Chemical Society[6]. When such reagents are not available, ascertain that they do not lessen the accuracy of the determination.

6.6.1 Potassium Iodide (KI) - Reagent grade KI often contains a reducing agent to prevent the oxidation of iodide to iodine on standing. KI meeting USP specifications usually contains little or no reducing agent. While this agent keeps the KI from turning yellow, it interferes significantly with oxidant and ozone measurement and calibration. Every lot of KI purchased should be tested before use. To test, prepare a 10% solution as directed in 6.9.1, Step 2, in a clear 100 ml volumetric flask. Make sure the pH is between 6.5 to 7.0. Add 0.10 ml of iodine working solution (Item 6.6.11) and mix well. Observe the iodine color visually or transfer 10 ml to a cuvette and read at 352 nm in the spectrophotometer. When reducing agent is present, the absorbance will fade within minutes. Add $\sim$ 10% hydrogen peroxide (H_2O_2) solution dropwise (with a graduated pipet or buret) to the 10% KI until the loss of absorbance stops. To check the end-point, again add 0.10 ml of the I_2 solution (Item 6.6.11). The color should not fade. Based on the volume V_1 of the H_2O_2 required, determine the volume V_2 of the H_2O_2 needed to neutralize the reductant in 1 liter of 50% KI (Item 6.6.9).

$$V_2 = (V_1)\,\frac{(50\%)}{(10\%)}\,\frac{(1000\ \text{ml})}{(100\ \text{ml})} \qquad (2)$$

Add V_2 ml H_2O_2 to each liter of the 50% KI 6.6.9 prepared. Verify that the proper amount of H_2O_2 has been added to the batch. A yellow color indicates too much H_2O_2 was added and a new batch should be prepared. When the solution is colorless, add 0.1 ml of the I_2 working solution (Item 6.6.11) forming a slight yellow color that should not fade. When it does, determine the additional amount of H_2O_2 required. Other KI solutions (1%) should be tested and treated in a similar manner.

6.6.2 Distilled Water - Double-distilled water should be used for all reagents. It can be prepared in an all-glass still. Before the second distillation, add potassium permanganate to the water to produce a faint pink color and one crystal of barium hydroxide per liter to make the water alkaline.

6.6.3 Absorbing Solution (1 % KI in 0.1 M phosphate buffer) - Dissolve 13.6 g of potassium dihydrogen phosphate (KH_2PO_4), 14.2 g of disodium hydrogen phosphate (Na_2HPO_4) or 35.8 g of the dodecahydrate salt ($Na_2HPO_4 \cdot 12\ H_2O$), and 10.0 g of KI in sequence in approximately 750 ml distilled water, and dilute to 1 liter. Keep at room temperature for at least one day before use. Measure the pH and adjust to 6.8 ± 0.2 with NaOH pellets or 10% H_3PO_4. This solution can be stored for several months in a glass-stoppered brown bottle at room temperature without deterioration. It should not be exposed to direct sunlight.

6.6.4 Standard Arsenious Oxide As_2O_3 Solution (0.05 N) - Dry reagent grade As_2O_3 at 105° to 115°C for one hour immediately before using. Cool to room temperature in a desiccator. Accurately weigh 2.473 g in a small glass-stoppered weighing bottle. Dissolve in 25 ml 1 N NaOH in a flask or beaker on a steam bath. Add 25 ml 1 N H_2SO_4. Cool, transfer quantitatively to a 1000 ml volumetric flask and dilute to volume. The solution should be neutral to litmus.

$$\text{Normality of } As_2O_3 = \frac{(\text{wt. } As_2O_3)}{(49.46)\ (1000)} \qquad (3)$$

6.6.5 Starch Indicator Soulution (0.2%) - Triturate 0.4 g soluble starch and approximately 2 mg mercuric iodide (preservative) with a few ml of water. Add the paste slowly to 200 ml boiling water. Continue boiling until the solution is clear, allow to cool, and transfer to a glass-stoppered bottle. Alternatively, a commercial indicator (Thyodene[a]) can be used.

6.6.6 Stock Iodine Solution (0.05 N I_2)

1. Preparation - Successively dissolve 16 g KI and 3.173 g resublimed I_2 in 25 ml distilled water. When the I_2 dissolves, transfer the solution to a 500 ml glass-stoppered volumetric flask. Dilute to volume with distilled water and mix thoroughly. Keep at room temperature at least one day before use. Store the solution in a dark brown, glass-stoppered bottle away from light. Re-standardize before use.

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[a] Indicator, Thyodene, Cat. No. T-138, Fisher Scientific Company

2. Standardization - Accurately pipet 20.0 ml of standard As_2O_3 solution (Item 6.6.4) into a 300 ml iodine flask and acidify with one drop of 10% H_2SO_4 solution. Add about 2 g solid sodium bicarbonate ($NaHCO_3$), and 5 ml starch solution (or 0.1 to 0.5 gm thyodene) as indicator. Titrate with the stock I_2 solution adding 1 ml of 10% H_2SO_4 near the end-point to saturate the solution with carbon dioxide. Continue the titration until a pale blue color is obtained that persists for 30 sec. Calculate the normality of the stock I_2 by equation 4.

$$\text{Normality } I_2 = \frac{\text{ml } As_2O_3 \text{ X normality } As_2O_3}{\text{ml } I_2} \quad (4)$$

The stock I_2 solution may also be standardized with 0.025 N sodium thiosulfate ($Na_2S_2O_3$). The $Na_2S_2O_3$ solution is in turn standardized with primary standard potassium biiodate ($KH(IO_3)_2$)[7] or potassium dichromate ($K_2Cr_2O_7$)[8].

6.6.7 Zero Air - This may be obtained from cylinders of high-pressure, compressed synthetic air, or by filtering ambient air. The air for generating and diluting the test gas should be free of ozone and any substances that will in any way a) change the test gas concentration, b) interfere in the analyzer response or c) interfere in the referee procedure. An activated carbon filter will remove most interferents, but when nitric oxide or sulfur dioxide is present in the ambient air, a CrO_3 oxidizer followed by a soda lime or triethanolamine filter is necessary to remove them. See Chapter 5, Gas Generation, for details.

6.6.8 0.5 M Buffer Solution (for static calibration) - Dissolve 71 g (0.5 mole) anhydrous Na_2HPO_4 or 179 g $Na_2HPO_4 \cdot 12\ H_2O$, and 68 g KH_2PO_4, in approximately 750 ml distilled water. Make up to almost one liter. Measure the pH. When different from pH 6.8 to 7.0, adjust with NaOH or KOH pellets, granular KH_2PO_4 or 10% H_3PO_4. Dilute to one liter. Store in an amber bottle and out of direct sunlight. Discard after two years. When exposure to sunlight is unavoidable, add 0.025 gm of a non-reducing preserving agent, e.g., sodium o-phenylphenate, sodium pentachlorophenate, Trichlorophenate (Dowicide B).

6.6.9 50% Alkaline KI Solution (for static calibration) - Dissolve 500 g of KI (See 6.6.1) in approximately 750 ml of water. Add a sufficient amount of concentrated NaOH solution or NaOH pellets to obtain a pH 9 to 11 and make up to one liter. Mix well and store in an amber bottle out of direct sunlight. Discard after two years.

6.6.10 Iodine Dilute Solution (0.004N I_2) - Transfer 40.00 ml of the 0.05 N I_2 stock solution (Item 6.6.6) to a 500 ml low-actinic volumetric flask with a volumetric pipette. Dilute to volume with distilled water. Mix well and store out of direct sunlight. Discard after two days. Calculate the normality of the I_2 by equation 5:

$$\text{N of dilute } I_2 = \frac{(40.00\text{ ml})\ (\text{N of stock } I_2)}{(500\text{ ml})} \qquad (5)$$

6.6.11 Iodine Working Solution (0.0008N I_2: equal to 10 μl O_3/ml of solution) - Calculate the volume V_d of dilute I_2 (Item 6.6.10) necessary to make 250 ml of iodine working solution by equation 6:

$$V_d = \frac{0.204}{\text{N of Dilute } I_2} \qquad (6)$$

where 0.204 is a combined constant (See Basis for calculations, 6.11).

Transfer the volume of 0.002 N I_2 solution calculated by equation 6 to a 250 ml low-actinic volumetric flask and dilute to volume with distilled water. Mix well and store out of direct sunlight. Prepare daily.

6.7 SPECTROPHOTOMETER CALIBRATION

1. Prepare a series of calibrating solutions between 0.1 to 0.7 μl O_3/ml by diluting aliquots (i.e., 1, 2, 3 ml) of the I_2 working solution (Item 6.6.11) to 100 ml with the 1% KI absorbing solution (Item 6.6.3). Obtain the spectrophotometer readings at 352 nm. Plot the absorbances versus equivalent μl O_3 per ml on rectilinear graph paper as a check for linearity. Calculate the slope b of the best-fit curve for the data using the method of least squares[b].

2. When a static calibration is to be performed on a colorimetric instrument using iodide absorbing solution, prepare a calibration

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[b] See Table 4-V in Chapter 4.

curve for the spectrophotometer as in step 1 above but using the same reagent formulation as used in the analyzer. This curve will be used when performing a secondary check on the accuracy of the calibrating solutions during static calibration (6.9).

6.8 DYNAMIC CALIBRATION

6.8.1 General

1. When a static calibration (6.9), is to be performed on the analyzer, it should be done before the dynamic calibration (6.8) to assure proper operation of its detection and signal presentation components.

2. When the analyzer to be calibrated has been operating as a continuous monitor, it is useful to determine the response near the span level first without changing the span setting (auditing). When the analyzer response is within 10% of that obtained in the previous calibration, the calibration is still valid and a new calibration is not needed. When the response is greater than 10% from the previous calibration proceed with the complete calibration. The audit data provide a record of the calibration drift. Instruments with non-linear response require the full calibration.

3. The static and dynamic responses may be compared (reconciled) to verify the proper operation of the analyzer. See 6.10 for details.

6.8.2 Procedure

1. The analyzer should be in good operating condition and installed in accordance with manufacturer's instructions. Operate the analyzer for at least 24 hours to warm-up. This 24 hour warm-up time may be shortened when so stated in the operating instructions. Adjust air and reagent flows to their recommended rates or the rates determined from the static calibration data and verify the flowrates as described in 6.5, Item 6. Record data only after stable response has been attained. Refer to 4.1.6 in Chapter 4 for determining stable responses.

2. Place the ozone generation apparatus (Item 6.5.1) as close as practical to the analyzer to prevent losses and to minimize pressure changes in the analyzer sampling duct. Determine the sample airflow requirements of the analyzer(s) and add the airflow (1.0 ℓ/min) needed for the referee analysis. Add about 10% of the total to insure an excess. (NOTE: The excess ozone stream should be vented or absorbed by a charcoal filter to avoid exposure to personnel.) In a proper assembly, connection or disconnection of the analyzers sampling ducts should not alter the airflow settings of the instruments.

3. The ozonizer lamp and power supply should be sufficiently warmed up to insure a steady ozone output. Some commercial ozone generators may require up to two hours for warm-up. With the ozonizer power supply on and the lamp completely shielded, flush the system with zero air for several minutes to remove residual ozone.

4. When a steady analyzer reading is obtained, pipet 10 ml of the 1% KI absorbing reagent (Item 6.6.3) into each of the 2 impingers. Assemble the impingers and connect to the sampling train as shown in Figure 6-III. Draw a sample from the sampling manifold through the train at 1.0 liter/min for 30 minutes. Allow the solutions to stand for 15 minutes. Transfer the exposed solution from each impinger, in turn, to a clean spectrophotometer cuvette and determine the absorbance of the solution at 352 nm against unexposed absorbing reagent as the reference blank.

   When the absorbance of the solution in the first impinger is greater than the blank, continue flushing the apparatus until the absorbance obtained is the same as the blank. NOTE: Inability to obtain a reading equal to the blank indicates possible presence of oxidants in the zero air or low pH (<6.5) of the absorbing solution. Correct problem(s) before continuing.

Zero the analyzer by adjusting the analyzer zero controls so that the output reads zero or reads the desired baseline value.

5. Generate an ozone gas concentration equal to 80 ± 5% (span gas) of the analyzer's full scale measuring range. When the analyzer response is steady, collect two samples of the gas stream and analyze as described in Step 4 above. Adjust the sampling period so that the absorbance of the sampling solution is about midscale (between 0.2 to 0.5) on the spectrophotometer. Five to ten minutes are usually sufficient. Do not exceed 30 minutes to avoid iodine losses.

6. Add the two spectrophotometer readings to obtain total absorbance. From the volume of air sampled and the slope of the spectrophotometer calibration curve (See Step 1 in 6.7), calculate the ppm O_3 (or $\mu g\ O_3/m^3$) by equation 7:

$$\text{ppm } O_3 = \frac{(A)\ (10\ \text{ml})}{(b)\ (V_a)} \qquad (7)$$

where: A = absorbance of the solution

b = slope of the spectrophotometer calibration curve obtained in 6.7

V_a = volume in liters of sample collected (liters/min X min)

To convert ppm (μl/l) to μg O_3/m^3, use equation 8.

$$\mu g\ O_3/m^3 = (1960)\ (ppm\ O_3) \qquad (8)$$

Usually, the change in the gas volumes of the samples due to deviation from the standard conditions of 25°C and 760 torr are small and may be neglected. When the deviations are large (sufficient to cause a change in gas volume greater than about 5%) correction should be made.

7. The concentrations of the two samples obtained should be within ± 5%. Differences greater than 5% indicates possible unstable gas concentrations or error in the sample collection and analysis. Correct these problems before proceeding with the calibration.

8. Determine the net analyzer reading by subtracting the analyzer baseline reading from the span reading.

9. Adjust, when possible, the analyzer upper limit (span) controls to give a reading equivalent to the span concentration (spanning). When the instrument has no span controls, proceed to Step 10 below. Generate zero air and note the analyzer reading. When the reading is different from the original reading by ≥ 2%, reset the analyzer to the original baseline and repeat Steps 5 through 9 above. NOTE: When the span and zero controls are not electrically independent, it may be necessary to rezero and respan iteratively until the proper zero and span settings are obtained.

10. Generate, in turn, four additional ozone concentrations (10, 20, 40 and 60% of full scale) and determine the ozone concentrations in duplicate as described in Steps 4 through 8 above. Record the net analyzer readings by subtracting the baseline reading from the individual readings.

6.8.3 Treatment of Dynamic Calibration Data

1. Plot the net analyzer readings on the vertical axis versus the ozone concentrations on the horizontal axis of an appropriate graph paper (rectilinear, log, semi-log, etc.). Calculate the slope b_d of the calibration curve that fits the points best by the method of least squares[b]. To determine the linearity of the response, see Test 4.5 in Chapter 4. A non-linear response from an instrument normally linear indicates malfunction in the analyzer or error in the calibration process. Correct problem(s) before recalibrating.

2. When a non-linear response is normal, draw a smooth line that fits the calibration points best. From this, prepare a template to transform the net analyzer readings to concentration units.

6.9 STATIC CALIBRATION

The following section pertains to calibration of continuous analyzers using neutral 10% KI as the absorbing reagent. See also 6.1.4. The procedures can also be used on other colorimetric KI instruments by using the appropriate reagent formulations.

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[b] See Chapter 4, Table 4-V.

6.9.1 Procedure

1. Turn the analyzer air and liquid pumps off. Clamp off and disconnect the reagent line at the air-liquid separator or other convenient place. Install a 125 ml low-actinic separatory funnel supported by a ring stand and connect the funnel to the inlet of the analyzer sample cell with 8 mm ID glass tubing. Butt-join the tubing with polyvinylchloride tubing. Disconnect the sample cell exit line at the inlet to the reagent reservoir and lead the line to a waste bucket.

   When the analyzer uses a solution reference, disconnect the reagent line at the exit port of the reference cell and recycle the solution back to the reagent reservoir so that the reagent flows through the reference cell only. Turn the analyzer reagent pump on.

2. Prepare 10% KI absorbing solution blank by placing 20 ml of the 0.5 M buffer reagent (Item 6.6.8) and 20 ml of the 50% alkaline KI reagent (Item 6.6.9) in a 100 ml low-actinic volumetric flask. Dilute to volume with distilled water and mix well.

NOTE: This, and all subsequent 10% KI solutions should be prepared as needed and used within minutes to prevent interference from oxidation of iodide to iodine by exposure to air or light.

3. Rinse the separatory funnel, connecting lines and sample cell with a small portion (≈ 10 ml) of the 10% KI blank solution twice. Fill the separatory funnel with the remainder of the reagent and adjust the flow through the sample cell to approximately the flow rate at which the instrument is to operate (1 ml/min ≈ 20 drops/min). The separatory funnel stopcock may be used to control the flow. When the analyzer reading is stable, set the recorder baseline slightly above the pen indicator stop (or zero) to permit indication of negative deviations from zero. Record the analyzer baseline reading and the position of the zero control.

4. Prepare a calibrating solution equal to about 80 ±5% of full scale with the 10% KI solution as follows: Make up 100 ml of 10% KI solution and mix well. Transfer a portion to the cuvette to zero the spectrophotometer at 352 nm. For a full scale of 1 ppm, 80% of full scale is 0.80 ppm O_3.

$$V_w = (V_c) \frac{(C)}{(C_w)} \qquad (9)$$

where: V_w = volume (ml) of iodine working solution (6.6.11)
V_c = volume of calibrating solution (100 ml)
C = concentration desired, in $\mu l\ O_3/ml$
C_w = concentration of working solution (10 $\mu l\ O_3/ml$)

For example: When the desired calibrating solution is 0.20 $\mu l\ O_3/ml$, the volume V_w of the iodine working solution required is:

$$V_w = (100\ ml)\ \frac{(0.20\ \mu l\ O_3/ml)}{(10\ \mu l\ O_3/ml)} = 2.0\ ml \qquad (10)$$

Pipette the required volume (8.0 ml) of the iodine working solution (6.6.11) to the remainder of the 10% KI in the volumetric flask. Zero the spectrophotometer with the reagent removed earlier then dilute the flask to volume with the same blank reagent. Mix well. This solution contains 0.80 $\mu l\ O_3/ml$. Discard the excess blank reagent in the cuvette.

5. Rinse the cuvette with some of the above solution. Read a portion of the solution in the spectrophotometer to verify that the solution contains 0.80 $\mu l\ O_3/ml$. When the proper reading cannot be obtained, check for error in the I_2 concentration, error in the dilution process or poor quality reagent. Correct problem(s) before proceeding with the calibration.

6. Rinse the separatory funnel with a small portion of the remaining 0.80 μl O_3/ml solution and fill the separatory funnel. Introduce the solution through the sample cell in the same manner as Step 3 above. Note the analyzer reading and adjust, when possible, the analyzer to give a reading equivalent to the span concentration (spanning). For instruments with non-linear response, proceed to Step 8 below.

7. Prepare and introduce blank 10% KI solution and note the analyzer reading. When the response is different from the original baseline by ≥ 2% of full scale, reset the analyzer to the original baseline and repeat Step 3 above. When the zero and span controls are not electrically independent, it may be necessary to rezero and respan iteratively until the proper zero and span settings are obtained.

8. Prepare, in turn, solutions equal to 10, 20, 40, and 60% of full scale (e.g., 0.10, 0.20 μl O_3/ml, etc.) and determine the analyzer response to each concentration as described in Steps 4 and 5 above.

9. Determine the net responses by subtracting the baseline reading from the individual readings. Replumb the analyzer to original operating condition.

6.9.2 Treatment of Static Calibration Data

1. Plot the net analyzer readings on the vertical axis versus μl O_3/ml of the calibrating solutions on the horizontal axis of an appropriate graph paper (rectilinear, semi-log, log, etc.). Calculate the slope b_s of the static response curve by the method of least squares[c]. To determine the linearity of the response, see Test 4.5 in Chapter 4. A non-linear response from an instrument normally linear indicates malfunction in the analyzer or error in the preparation of the calibrating solutions. Correct the problem(s) before recalibrating.

2. When a non-linear response is normal, prepare a template as directed in Step 2 of 6.8.3. An alternate method is to attempt to linearize the instrument output by adjusting the electronics of the photometer by some combination of photocell voltage and span upper-limit setting until a linear output is found over the concentration range of interest.

6.9.3 Determination of Sample Air Flowrate

For instruments not equipped with adjustable upper limit or span controls or when the range of span adjust is insufficient, the slope of the static calibration can be used to determine the sample airflow rate that will make the analyzer output correspond to the pollutant concentration or a simple fraction or multiple of the concentration as follows:

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[c] See Table 4-V in Chapter 4.

$$Q_a = (Q_r)\,\frac{(f)}{(b_s)} \qquad (9)$$

where: f = fraction or multiple of the analyzer range desired. (e.g., 0.5, 1, 2, 3)

Q_a = airflow rate, ml/min

Q_r = reagent flowrate, ml/min

b_s = slope of the static calibration curve obtained in 6.9.2

6.10 RECONCILING STATIC AND DYNAMIC CALIBRATIONS

1. The static calibration slope b_s (6.9.2, Step 1) and dynamic calibration slope b_d (6.8.3, Step 1) are compared in equation 10 below.

$$R = \frac{|b_s - b_d|}{b_s} \times 100 \qquad (10)$$

2. Large values of R ($\geq$ 10%) are indicative of a) error in the analyzer's air or liquid flowrate, b) leaks or malfunction in the analyzer, c) poor quality reagents and/or reactants, d) error in the static or dynamic calibration process/or e) change in efficiency of sample collection. Consult the analyzer operating instructions and/or the manufacturer and correct problem(s) before recalibrating.

6.11 BASIS FOR CALCULATIONS

The relationship between the standard iodine and ozone and the constant used in equation 6 (6.6.11) was obtained from the stoichiometric equation 1. One mole of ozone produces one mole of iodine according to the reaction:

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \qquad (1)$$

One mole of ozone, however, contains two equivalents (there is a two electron exchange in the half reaction):

$$O_3 + H_2O + 2e^- \rightarrow 2OH^- + O_2 \qquad (11)$$

Therefore, one-half mole of ozone is equal to one equivalent (eq.) of iodine. Since one mole of ozone occupies, at 25°C and 760 torr, 24.46 liters, then

$$1 \text{ eq. } O_3 = 12.23 \text{ liter } O_3 = 1 \text{ eq. } I_2$$

or

$$12.23 \text{ ml } O_3 = 1 \text{ milliequivalent (meq) } I_2$$

therefore

$$10\ \mu l\ O_3 = \frac{10}{12.23}\ \mu eq\ I_2 \qquad (12)$$

$$= \frac{10 \times 10^{-3}}{12.23}\ meq\ I_2 \qquad (13)$$

or in terms of solution:

$$10\ \mu l\ O_3/ml = 0.8177 \times 10^{-3}\ \text{meq}\ I_2/ml \qquad (14)$$

The volume V_d, in ml, of the dilute iodine solution N_d needed to make 250 ml of a working solution N_w equal to 10 µl O_3/ml is then:

$$V_d\ N_d = V_w\ N_w \qquad (15)$$

or

$$V_d = V_w \frac{N_w}{N_d} = \frac{(250\ ml)\ (0.8177)\ (10^{-3})}{(N_d)} \qquad (16)$$

then

$$V_d = \frac{0.204}{N_d} \qquad (17)$$

which is the basis for the constant in equation 6.

6.12 REFERENCES

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7. G Fredrick Smith Chemical Co., Columbus, OH 43223

8. JT Baker Chemical Co., Phillipsburg, N.J. 08865

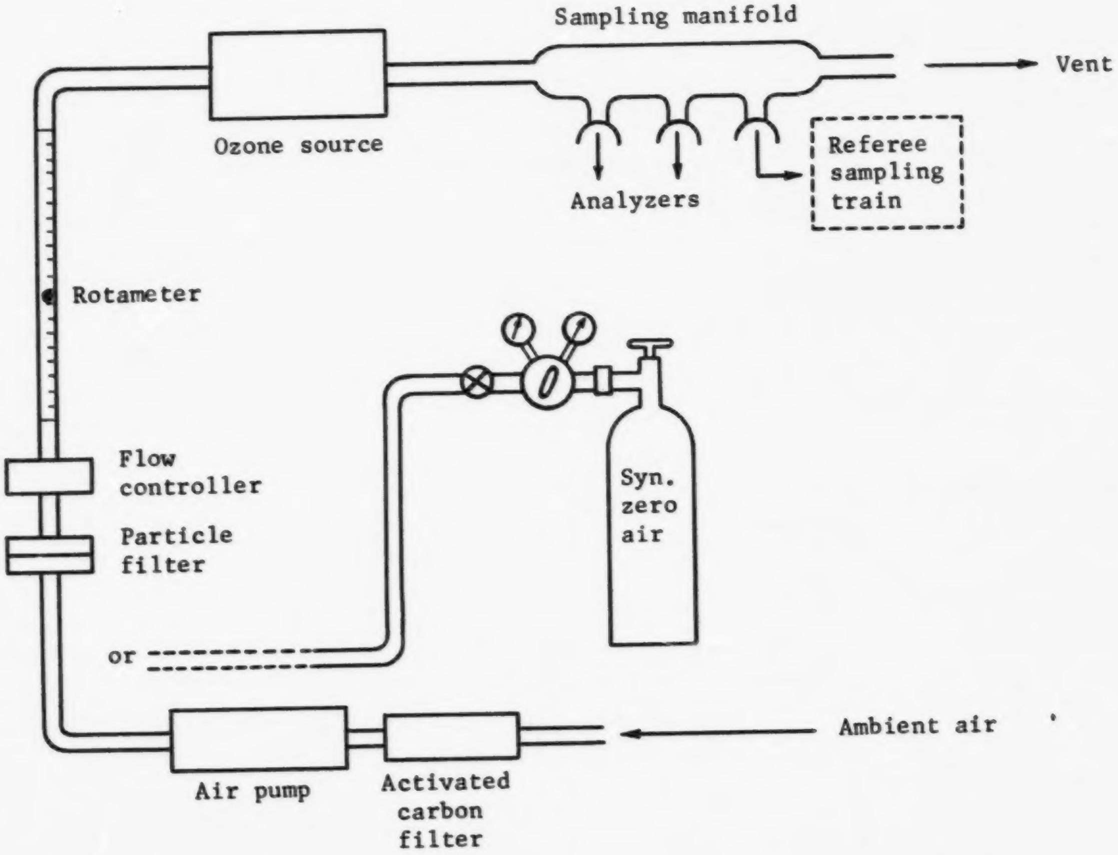
Sampling manifold
Vent
Ozone source
Analyzers
Referee sampling train
Rotameter
Flow controller
Particle filter
Syn. zero air
or
Air pump
Activated carbon filter
Ambient air

Figure 6-I. Gas generating apparatus for calibrating ozone analyzers.

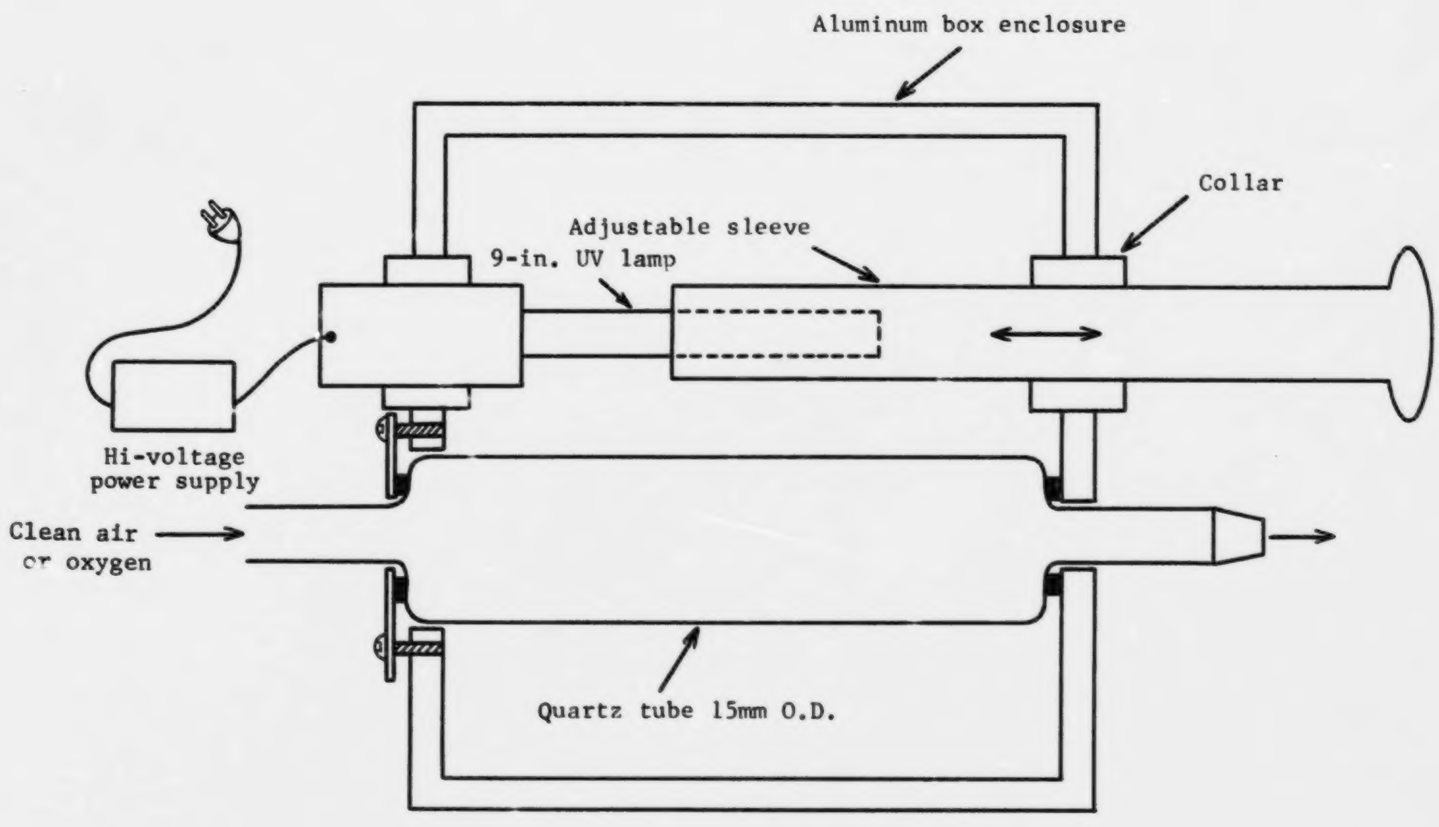
Aluminum box enclosure
Collar
Adjustable sleeve
9-in. UV lamp
Hi-voltage power supply
Clean air or oxygen
Quartz tube 15mm O.D.

Figure 6-II. Ozone generator.

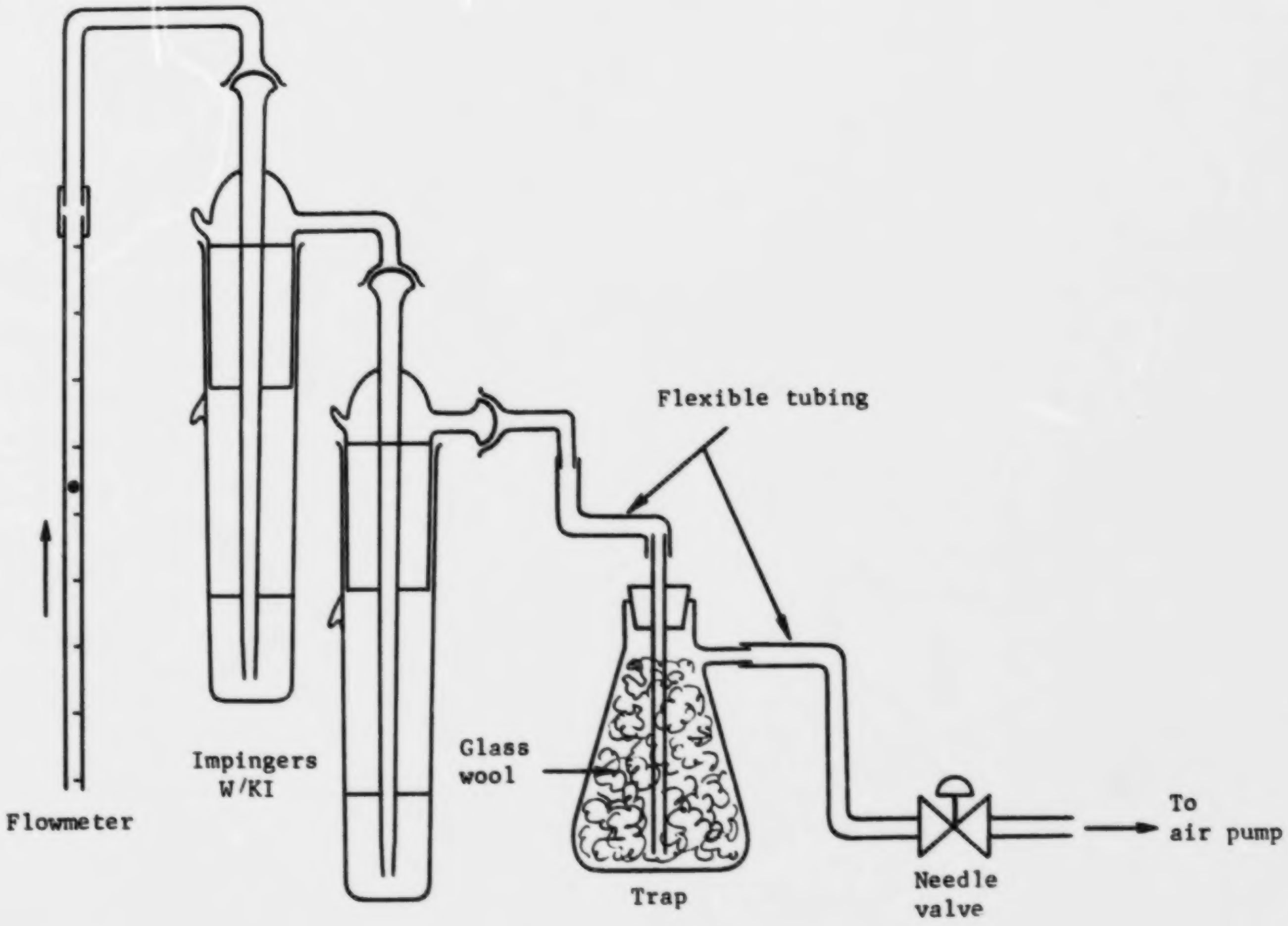
Flexible tubing
Impingers
W/KI
Glass
wool
Flowmeter
Trap
Needle
valve
To
air pump

Figure 6-III. Sampling train for referee ozone analysis.

7.0 CALIBRATION PROCEDURE FOR AUTOMATED ATMOSPHERIC NITROGEN DIOXIDE AND NITRIC OXIDE ANALYZERS

7.1 PRINCIPLE AND SCOPE

7.1.1 This procedure is for the calibration of continuous analyzers used for monitoring atmospheric concentrations of nitrogen dioxide (NO_2) and nitric oxide (NO). Analyzers for monitoring both pollutants concurrently are common. The calibration may be of two types, dynamic and static. The dynamic calibration must always be done and is performed by determining the analyzer response to a series of NO or NO_2 concentrations. The dynamic calibration is applicable to all NO, NO_2 or NO_x, analyzers and is a performance test of the entire instrument under simulated service conditions. The static calibration is performed by determining the analyzer response to artificial stimuli such as standard calibrating solutions, optical filters, screens, electrical signals, resistors, etc. This calibration is primarily applicable to analyzers using wet-chemistry and colorimetry and is a test of the detection and signal presentation components only. It is not a substitute for the dynamic calibration.

7.1.2 Each calibrating gas for the dynamic calibration is generated by mixing a dilute NO or NO_2 gas stream or diluting with clean air a concentrated source such as NO_2 from a permeation tube or from a cylinder. Each gas is sampled simultaneously with the analyzer and with referee methods[1,2] to establish the gas concentrations.

7.1.3 The static calibration is accomplished by adding known concentrations of sodium nitrite to measured volumes of the analyzer absorbing solution. The solutions produce colors with absorbances equivalent to concentrations of NO_2. These solutions are flowed through the analyzer's detector at the reagent flow conditions encountered during normal operation. The analyzer readings are plotted versus NO_2 concentrations to obtain the static calibration curve. The instrument variables, e.g., air and liquid flow rates, may be adjusted after static calibration to make the output response conform to the pollutant concentration or a simple multiple or fraction of the concentration in parts per million (ppm) or micrograms per cubic meter ($\mu g/m^3$) (spanning). When a static is not performed, the spanning may be done during the dynamic calibration.

7.2 RANGE

The range of the calibration procedure is determined by that of the referee method. For a 4-liter sample collected in 10 ml of absorbing solution and measured in a 1.0 inch cuvette, the range is between 0.01 to 2ppm (10 to 3,760 $\mu g\ NO_2/m^3$ and 12 to 2,450 $\mu g\ NO/m^3$)[3]. The sampling rate may be reduced or the sampling period increased or decreased to extend or reduce the range.

Continuous colorimetric analyzers for NO_2 and NO usually measure these gases in the same range. The linear range for chemiluminescent NO-NO_2 analyzers is about 0.005 to 15 ppm (9 to 28,000 $\mu g\ NO_2/m^3$ and

6 to 18,400 μg NO/m^3)[4]. Amperometric analyzers usually measure concentrations from 0.005 to 1 ppm (9 to 1,880 μg NO_2/m^3; 6 to 1,220 μg NO/m^3). Sampling rates of these instruments range from 0.15 to 4 l/min.

7.3 INTERFERENCES

7.3.1 The main interference arises from traces of NO in NO_2 and vice versa. Zero air and pure streams of NO or NO_2 can be obtained by the use of various combinations of chemical absorbers and converters[2,5,6]. Details for preparing these absorbers are given in Table 5-III, Chapter 5.

7.3.2 Relative humidities in excess of 90% for extended periods (> 3 hr) inactivate the chromium trioxide oxidizer used for converting NO to NO_2 in the manual referee analysis and in some analyzers. Operating the oxidizer 5°C above ambient temperatures (e.g., by heating with a 7 W lamp) usually eliminates this problem.

7.4 PRECISION, ACCURACY, AND STABILITY

7.4.1 A coefficient of variation of 1% can be achieved in the manual referee analysis with careful work[7]; the limiting factors are in the difficulty in measuring the volumes of the air samples and in reading the absorbance of the colored reagent. Instrumental precision will usually decrease between 2 to 5% because of airflow variations. These variations are produced by pressure changes and unstable or pulsating flows.

7.4.2 When spanning is possible, any discrepancy between the input and output may be resolved by adjusting the instrument output to correspond to the value of the calibrating gas or solution. Where analyzers have no span controls, a correction factor may be calculated to convert the analyzer readings to pollutant concentrations.

7.4.3 The absorbing solution used in the manual referee procedure or the static calibration should be protected from direct sunlight. Allow 15 minutes for maximum color development and measure the absorbance within one hour after sampling to minimize any color loss.

7.4.4 A detailed discussion of the various sources of error in calibrating gas preparation is given in Reference 1, Part I: General Precautions and Techniques. The minimization of the sources of error is important to assure high levels of accuracy and precision.

7.5 APPARATUS

A gas generating system (Figure 7-I) capable of providing calibrating gases in the range of 0.01 to 2 ppm (19 to 3,760 μg NO_2/m^3 or 12 to 2450 μg NO/m^3) is needed in the dynamic calibration. The system consists of a gas dilution apparatus, sources of zero air and NO and NO_2 gases and a sampling train (Figure 7-11) for referee analysis. The components and connecting lines used should be sized and assembled so that the differences in the pressure between the various flow components do not exceed 2% overall to prevent errors in flowrate measurements.

7.5.1 Gas Dilution Apparatus

1. Flowmeters - Rotameters with sapphire or stainless steel balls are used to measure the flow of zero air (0 to 5 liter/min) and pollutant gas (0 to 1 liter/min). They should be calibrated frequently (at least once a month), with an appropriate flow measuring device such as a wet test meter, dry gas meter, soap bubble meter or calibrated rotameter.

2. Connecting gas flow lines - Use 8 mm ID (minimum) borosilicate glass tubing or 10 mm ID polytetrafluoroethylene (TFE) tubing for all connections. Flexible polyvinyl chloride (PVC) tubing may be used to butt-join sections of inert tubings only. Ball and socket joints (e.g., 12/5 mm) with 8 mm stems are preferred for connections that are frequently made and broken such as the calibrating gas lines to the dilution apparatus and the sampling ducts to the analyzer(s).

3. Mixing chamber - A cylindrical Kjeldahl type connecting bulb of 200 to 300 ml volume works well. This can also be fabricated

from borosilicate glass as shown in Figure 7-I, with standard 12/5 mm ball connections.

4. NO Oxidizer (CrO_3): Fill a 100 to 150 by 15 mm ID glass tube with ball connecting ends (see Figure 7-I) to a length of 20 to 80 mm with CrO_3 granules (Item 7.6.6). Use glass wool plugs to hold granules in place. (Caution! Protect eyes and skin when handling this material. Do not breathe the oxidizer dust.) Before use, pass air containing 30 to 70% RH at 0.5 l/min about 1 hr. to condition. Discard when more than 3/4 of the packing bed depth turns brown.

5. Timer, 0 to 30.0 minutes - for measuring the sampling period in the referee method.

7.5.2 Zero Air Source

The air for diluting the calibrating gases should be free of NO and NO_2 and substances that will in any way 1) change the calibrating gas concentration, 2) interfere in the analyzer response or 3) interfere in the referee procedure. The zero air may be furnished from a gas cylinder or by filtering ambient air as indicated in Figure 7-I.

1. Cylinder Zero Air - Cylinders should be fitted with a two-stage pressure regulator and with fine control needle valves. A NO_x filter (Item 3a) is used when NO_x contaminants are present.

The humidifier (Item 3b) should be used with a pressure relief valve set between 2 to 5 psig (1.4 to 3.4 newton/cm^2) to prevent expolsion of glass vessel in case of flow stoppage.

2. Air Pump (for transport of ambient air) - An oil-less (carbon vane or diaphragm) air pump capable of delivering between 5 to 10 liters/min is used. The pump is fitted with a vibration pad, a fine control needle valve, and a bleed-off valve. A particle filter should be installed downstream of carbon vane pumps and is optional with diaghragm types.

3. Air Filter

   (a) NO_x filter - This is used to remove any NO and NO_2 from the air used for zero air. Fill a 30 mm OD by 300 mm long glass tube to one-half its volume with CrO_3 oxidizer (Item 7.6.6) and the rest with soda lime (Item 7.6.5). Place the soda lime on the downstream side of the CrO_3. Use glass wool plugs in both ends to retain the granules. The orange CrO_3 granules turns brown with use. Discard when more than 3/4 of the packing length is brown.

   (b) Humidifier - This is used to humidify the zero air for the proper operation of the CrO_3 oxidizer (7.5.1, Item 4 and Item 3a) and consists of a 250 ml flask with the inlet tube extending to 2 cm above water level as shown in Figure 7-I to give a relative humidity of 70 to 80%. Install upstream of the NO_x filter (Item 3a) and the air pump (Item 2) and downstream of the charcoal filter (Item 3c).

(c) Charcoal Filter - See Item 2 in 5.2.2 and Table 5-III for requirements and preparation.

7.5.3 NO_2 Permeation Apparatus

Proper operation of permeation devices or tubes (Item 7.6.2) requires a constant temperature bath maintained within 0.1°C at 20 to 30°C and equipped with a temperature conditioning coil and permeation tube holder. The gas permeation systems described for SO_2[8] are also applicable for NO_2 generation[9]. Commercial systems are available.

7.5.4 Ozone Generator (when calibrating chemiluminescent analyzers)

An ozone generator is used in the zero air line to furnish ozone for converting NO to NO_2. This provides a mixture of NO and NO_2 which is used to test the efficiency of the NO_2-to-NO converter in chemiluminescent analyzers[10]. See 7.8.5 for details. Ozone generators for conversion of NO to NO_2 are commercially available. One can also be fabricated by using a low pressure mercury lamp (Ultraviolet Products, Inc., San Gabriel, Cal., or equivalent) and a lamp power supply. See 6.5.1 in Chapter 6 for details.

7.5.5 NO$_2$ Absorber (TEA) - Fill a 20 mm ID by 100 to 150 mm long polyethylene tube with tubing fittings at both ends with TEA granules (Item 7.6.4). Hold the granules in place with glass wool plugs. Install the absorber in the line between the NO source tank and the dilution apparatus.

7.5.6 Spectrophotometer or colorimeter - With 2.54 cm (1 inch) cuvettes for measuring the absorbance at 550 nm.

7.5.7 Manual Sampling Train:

Assemble the sampling train as shown in Figure 7-II. Use ground-glass joints upstream from the bubbler. Other connections may be butt-joined with polyvinylchloride tubing.

1. Absorber - All-glass bubbler with a maximum frit pore diameter of 60μ as shown in Figure 7-II or in References 1 and 2 are needed to collect the samples for referee analysis. Bubblers may be purchased from suppliers of air pollution equipment and many glassware suppliers. Ball-joint connections are recommended for convenience.

2. Air-vacuum Pump - Capable of drawing 0.40 liter/min through the bubbler. The pump should be equipped with a needle valve and trap at the inlet side to regulate flow.

3. Flowmeter - Calibrated to measure gas flows of 0.5 to 2 liters/min within ± 2%. See Item 1 in 7.5.1 for calibration requirements.

4. Trap - A vessel containing glass wool to protect needle valve from moisture.

7.5.8 Miscellaneous: Other equipment needed to perform the manual reference sampling operation described in Reference 1 and 2.

7.5.9 Calibrating Solution Dispenser (for static calibration): A solution dispenser, consisting of one or two lengths (about 50 cm) of small diameter (about 1.5 mm I.D.) clear polyvinylchloride (PVC) tubing, a plastic anti-syphon device and a 125 ml low-actinic separatory funnel as shown in Figure 7-III, is used to deliver the calibrating solutions under controlled flow conditions by means of furnished screw clamp(s) on the tubing(s). This (hypodermoclysis) set, which is intended for administering fluids under the skin, is inexpensive and can be purchased from medical supply houses. A similar device can be fabricated from small diameter plastic tubing, Y connector and screw clamps.

7.6 REAGENTS AND GASES

Purity of Chemicals - Unless otherwise indicated, all reagents specifications shall conform to the Committee on Analytical Reagents of the American Chemical Society[11]. When such reagents are not available, ascertain that they do not lessen the accuracy of the determination.

7.6.1 Cylinder NO: A cylinder of compressed N_2 gas containing about 100 ppm NO (122 mg NO/m^3), <10 ppm H_2O and <3 ppm O_2: This mixture is quite stable when care is taken to exclude air during preparation. It may be purchased or can be prepared in the laboratory using a closed-system, vacuum-pressure manifold[12]. Further dilution of the gas brings the concentration within the normal range of NO_x analyzers.

Permeation tubes containing NO are not available because of its low boiling point (-152°C).

7.6.2 NO_2 Permeation Devices: Permeation devices containing NO_2 may be purchased[13,14]. Their use usually requires the use of a temperature controlled bath. While SO_2 permeation devices can be used as a primary standard because of their reliable emission rates, NO_2 permeation devices have not yet achieved the same level of reliability. The exact concentrations produced, therefore, must be established during calibration by a referee method[1]. Exposure of the tube to water vapor and wide variations in temperature during operation or storage may produce marked changes in permeation rates. NO_2 devices may also be used for calibrating NO analyzers when a NO_2-to-NO converter[4] is used.

7.6.3 Other Sources of NO and NO_2: Lower concentrations of NO and NO_2 in steel cylinders (about 1/10th of those listed in 7.6.1) may be used but since these substances are unstable at these low levels, the concentrations resulting from such mixtures must be determined by referee analysis just prior to and/or during calibration.

7.6.4 Triethanolamine (TEA): Soak 1.5 mm (1/16") diameter or 10 to 14 mesh granules of porous, inert material such as firebrick, alumina, or xeolites, in 20% aqueous TEA[6]. Drain, spread on a dish, and dry for 30 to 60 min at 90 to 95°C. The granules should be free flowing.

7.6.5 Soda Lime - Granules, 4-8 mesh.

7.6.6 Chromium Trioxide (CrO_3) Oxidizer[2,6] - Soak 15 to 40 mesh porous firebrick or alumina in a 16% w/w aqueous CrO_3 solution. Drain, spread on a dish and dry in an oven for 30 to 60 min at 105 to 115°C, then place the dish in a desiccator containing a saturated salt solution which maintains the relative humidity between 50 to 70%. The reddish color changes to a golden orange when properly equilibrated. Caution! Protect eyes and skin when handling this material. Do not breathe the oxidizer dust.

7.6.7 $NaNO_2$ Stock Solution: Dissolve 2.03 g $NaNO_2$ (a correction is applied if purity is less than 100%) in distilled water and dilute to 1000 ml in a volumetric flask. This solution contains the equivalent of 1000 μl NO_2/ml. The weight of the nitrite is calculated based upon the empirical observation that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide[1,15].

7.6.8 $NaNO_2$ Working Solution (10 μl NO_2/ml): Dilute 5.00 ml of the stock $NaNO_2$ solution (Item 7.6.7) to 500 ml with distilled water (nitrite free) in a low-actinic volumetric flask. This working standard is equal to 10 μl of NO_2/ml.

7.6.9 Additional Reagents: Reagents needed to perform the manual referee analysis are described in Reference 1.

7.7 SPECTROPHOTOMETER CALIBRATION

1. Prepare a series of calibrating solutions equivalent to between 0.04 to 0.20 μl NO_2/ml by diluting 1,2,3 ml etc of $NaNO_2$ working standard (Item 7.6.8) in 250 ml of the azo-dye absorbing reagent as directed in Reference 1 and in 7.9, Static Calibration. Allow 15 minutes for full color development and then read the solutions in the spectrophotometer at 550 nm. Plot the absorbances on the vertical axis versus μl NO_2/ml on the horizontal axis of a rectilinear graph paper as a check for linearity. Calculate the slope b of best-fit curve for the data using the method of least squares[a].

2. When a static calibration is to be performed on the analyzer and the formulation of the analyzer absorbing solution is different from that of the referee procedure, obtain a spectrophotometer calibration factor by diluting aliquots of the $NaNO_2$ working solution with the analyzer reagent as described in Step 1 above.

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[a] See Chapter 4, Table 4-V.

7.8 DYNAMIC CALIBRATION

7.8.1 General

1. When a static calibration (7.9) is to be performed on the analyzer, it should be done before the dynamic (7.8) to assure proper operation of its detection and signal presentation components. The static and dynamic responses may be compared (reconciled) to verify the proper operation of the analyzer. See 7.10 for details.

2. When the analyzer has been operating as continuous monitor, it is useful to determine the response near the span level first without changing the span settings (auditing). When the response is within 10% of the previous calibration, the calibration is still valid and a new calibration is not necessary. When the response is greater than 10%, proceed with the complete calibration. The audit data provide a record of the calibration drift. Instruments with non-linear response require the full calibration.

3. Chemiluminescent NO_x analyzers with single detectors that measure NO_2 by difference ($NO_2 = NO_x - NO$) are usually equipped with converters for reducing the NO_2 to NO. Such instruments must first be calibrated with NO because the analyzers response to NO_2 depend on the efficiency of the converters. See 7.8.5 for details.

4. The analyzer to be calibrated should be in good operating condition and installed in accordance with the manufacturer's instructions. Operate the analyzer for at least 24 hours to warm-up. This 24-hr warm-up period may be shortened when so stated in the operating instructions. Adjust the air and reagent flowrates to their recommended rates or to the rates determined from the static calibration (7.9) data and verify the rates as described in 7.5.1, Item 1.

5. Record all data only after stable analyzer response has been attained. Refer to 4.1.6 in Chapter 4 for determining stable response.

6. Assemble the gas generating system for generating NO or NO_2 as needed. Place the system as close as practical to the analyzer to prevent losses and to minimize pressure changes in the analyzer sampling ducts. Calculate the airflow of the analyzer(s) and add the airflow (400 ml/min) needed for the referee analysis. Add about 10% of the total to insure an excess. (NOTE: The excess calibrating gas should be vented or absorbed by a non-restricting filter to prevent exposure to personnel.) In a proper assembly connection or disconnection of the analyzer sampling line should not alter the airflow settings.

7.8.2 Analyzer Zero

1. Generate a flow of zero air equal to the rate determined in 7.8.1, Step 6 above and sample with the analyzer. When a stable analyzer reading is obtained, pipet 10 ml of the azo-dye absorbing reagent in the bubbler (7.5.7, Item 1)[1]. Assemble the bubbler and connect to the sampling train as shown in Figure 7-II.

   Sample the gas stream according to the manual referee method[1] for 10 minutes at 400 ml/min. Wait for 15 minutes for color development and then transfer the solution to a clean 1.0 inch (2.54 cm) cuvette. Measure the absorbance of the solution at 550 nm on the spectrophotometer against unexposed absorbing reagent as blank.

2. When the absorbance of the solution is greater than the blank, continue flushing the generation system until the absorbance obtained is the same as the blank. Inability to obtain a reading equal to the blank indicates interferents in the zero air. Correct the problem before proceeding.

3. Zero the analyzer by adjusting the analyzer controls so that the output corresponds to zero or the desired baseline value.

7.8.3 Generation of NO_2

1. Connect the source of the NO_2 (NO_2 permeation apparatus 7.5.3 or the NO cylinder 7.6.1 and ozone generator 7.5.4) as shown in the gas generation system (Figure 7-I). It may be necessary before hookup to bleed the cylinder outside the generation system at a low flow (30 to 50 ml/min) for one to two hours to condition the delivery tubing. (NOTE: Bleed the NO_2 into a filter to avoid exposure to personnel).

2. Generate a NO_2 concentration equal to 80 ± 5% (span gas) of full scale. When a steady analyzer reading is obtained, collect two samples of the gas stream and analyze as described in Step 1 of 7.8.2. Adjust the sampling period to keep the absorbance of the samples at about midscale (0.3 to 0.5 A) on the spectrophotometer. Five to ten minutes are usually sufficient.

3. From the volume of air sample and the slope of the spectrophotometer calibration curve, calculate the ppm NO_2 as follows:

$$\text{ppm} = \frac{(A)\ (10)}{(b)\ (V_a)} \qquad (1)$$

where: ppm = concentration (μ/l) NO_2 or NO in air

A = absorbance of the solution

b = slope of the spectrophotometer calibration curve obtained in 7.7.

V_a = volume, in liters, of the gas sample collected (liters/min X min).

To convert ppm to $\mu g/m^3$, use equation 2 for NO and equation 3 for NO_2

$$\mu g\ NO/m^3 = ppm\ NO \times 1230 \qquad (2)$$

$$\mu g\ NO_2/m^3 = ppm\ NO_2 \times 1880 \qquad (3)$$

Usually, the change in the gas volumes of the samples due to deviation from the standard conditions of 25°C and 760 torr is small and may be neglected. When the deviations are large (sufficient to cause a change ≥ 5% in gas volume), correction should be made.

4. The concentration of duplicate samples should be within 5%. Differences greater than 5% may be due to unstable gas concentration or error in sample collection and analysis. Correct these problems before proceeding with the calibration.

5. Determine the net analyzer reading by subtracting the baseline reading from the span reading.

6. When possible, adjust the analyzer to give a reading equivalent to the span NO_2 concentration obtained in Step 3 above (spanning). When the instrument has no span controls, proceed to Step 7 below. Generate zero air and note the analyzer reading. When the reading is different from the original baseline reading by ≥ 2%, reset the

analyzer to the original baseline and repeat Steps 2 through 6 above. NOTE: When the span and zero controls are not electrically independent, it may be necessary to rezero and respan iteratively until the proper zero and span settings are obtained.

7. Generate, in turn, four additional concentrations (10, 20, 30, 40 and 60% of full scale are suggested). Determine the NO_2 concentrations in duplicate as described in Steps 2 through 4 above. Record the net analyzer responses by subtracting the baseline reading from the individual readings.

7.8.4 Generation of NO

1. Install the TEA NO_2 absorber (Item 7.5.5) at the outlet of the NO (Item 7.6.1) cylinder to remove any traces of NO_2. Install the NO (CrO_3) oxidizer (Item 4 in 7.5.1) in the manual sampling train as shown in Figure 7-II. This oxidizes NO to NO_2 for referee analysis. The humidity of the gas stream is controlled by the humidifier in the zero air line as shown in Figure 7-I. Connect the cylinder of NO as shown in Fig. 7-I. The rest of the calibration follows the same procedure as described for NO_2 in 7.8.3 above.

2. Determine the NO concentration by equation 1 in Step 3 of 7.8.3. This procedure is valid because the conversion of NO to NO_2 is 100% when the CrO_3 is used as specified[6].

7.8.5 Determination of Converter Efficiency (for chemiluminescent analyzers)

1. To determine the converter efficiency of chemiluminescent NO_2 and NO_x analyzers, generate an NO concentration equal to 80 ± 5% of full scale. Verify the concentration and record the analyzer readings Y_{NO} and Y_{NO_x} in both the NO and NO_x modes.

2. Oxidize a portion of the NO to NO_2 by turning the ozone generator (Fig 7-I) on and adjust the ozone output so that the NO reading Y_{NO} is reduced to about one-half. Record the new NO and NO_x readings Y'_{NO} and Y'_{NO_x}.

   The decrease in the NO reading $(Y_{NO} - Y'_{NO})$ is equal to the input NO_2 concentration. The analyzer output as NO_2 is equal to the difference between the new NO_x and NO readings or $Y'_{NO_x} - Y'_{NO}$.

3. Calculate the conversion efficiency f_c by equation 5.

$$f_c = \frac{Y'_{NO_x} - Y'_{NO}}{Y_{NO} - Y'_{NO}} \qquad (5)$$

   A ratio f_c of the output NO_2 to the input NO_2 of less than 1.0 indicates the conversion is less than 100% and the converter should either be corrected or preferably replaced.

7.8.6 Treatment of Dynamic Calibration Data

1. Plot the net analyzer readings for each channel on the vertical axis versus the ppm NO_2 (7.8.3) or ppm NO (7.8.4) obtained by manual sampling on the horizontal axis of an appropriate graph paper (rectilinear, semilog, log, etc.). Calculate the slope b_d of best-fit curve for the data using the method of least squares[b]. To determine the linearity of the response, see Test 4.5 in Chapter 4. A non-linear response from an instrument normally linear indicates malfunction in the analyzer or error in the calibration process. Correct problem(s) before recalibrating.

2. When a non-linear response is normal, draw a smooth line through the calibration points that fits the data best. From this, prepare a template to convert the net analyzer readings to concentration units.

7.9 STATIC CALIBRATION

The following section pertains to colorimetric analyzers using azo-dye forming reagents for monitoring NO, NO_2 or NO_x. See also 7.1.3.

7.9.1 Procedure

1. The reagent used in the following procedure should be formulated in accordance with the manufacturer's recommendations.

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[b] See Chapter 4, Table 4-V.

2. Turn the analyzer air and liquid pumps off. Disconnect the reagent line at the exit port of the photometer reference cell and recycle the solution to the reagent reservoir. Disconnect the spent reagent line at the used-reagent reservoir, or at the inlet to the reagent recovery carbon column, when so equipped, and lead it to a waste bucket. Disconnect the reagent line at the sample cell inlet and connect the delivery end of a calibrating solution dispenser (Item 7.5.9). Support the separatory funnel near the instrument on a ring stand. Turn the analyzer reagent pump on. The reagent now flows only through the reference cell. Siphon absorbing solution from the analyzer reagent reservoir into six 250 ml low-actinic volumetric flasks and fill almost to the mark.

3. Mark one of the flasks as blank. Pour about 15 ml of the reagent from the blank into the separatory funnel. Squeeze out any air bubbles trapped between the funnel and the screw clamps. Open the screw clamp(s) and flush the connecting line and cell. Repeat with a second 15 ml portion. Fill the separatory funnel with the blank reagent and adjust the discharge rate into the cell at about the same flow rate at which the analyzer is to operate (1 ml/min equals about 20 drops/minute). For dual channel analyzer that monitor both pollutants (NO and NO_2) concurrently, Steps 3 through 8 can be performed simultaneously using the same calibrating solution for both channels.

4. While waiting for the instrument reading to stabilize, determine, by equation 6, the volumes of working $NaNO_2$ solution (Item 7.6.8) required (in 250 ml) to produce a series of calibrating standards equal to 10, 20, 40, 60 and 80% of full scale.

$$V_w = (v_c)\,\frac{(C)}{(C_w)} \qquad (6)$$

where: C = concentration (in µl NO_2/ml) desired

C_w = concentration of working solution (10 µl NO_2/ml)

V_c = volume of calibrating solution (250 ml)

Pipet the required volumes, e.g., 1.0, 2.0, into the five remaining 250 ml volumetric flasks containing the absorbing reagent. Dilute to the mark with the reagent and mix well. Let stand for 15 min for full color development.

Read the color of a portion of each standard solution with the previously calibrated spectrophotometer (Item 7.7) to verify that each standard contains the equivalent µl NO_2/ml calculated in Step 4. When the proper readings cannot be obtained, check for error(s) in the $NaNO_2$ concentration, error in the dilution process or poor quality reagent(s). Correct problem(s) before proceeding with the calibration.

5. After the analyzer response has stabilized on the blank reagent, adjust the analyzer controls to obtain the desired baseline reading.

6. Introduce the standard equal to 80% of full scale as directed in Step 3 above. When a steady reading is obtained, adjust, when possible, the analyzer reading to correspond to the concentration of standard. For instruments with no span controls, proceed to Step 8 below.

7. Introduce blank reagent and note the analyzer reading. When the reading is different from the original baseline by ≥ 2%, reset the analyzer to the original baseline and repeat Steps 3 and 5. When the span and zero controls are not electrically independent, it may be necessary to rezero and respan iteratively until the proper zero and span settings are obtained.

8. Introduce the remaining calibrating standards in turn and record the corresponding analyzer readings as described in Step 5. Determine the net readings by subtracting the baseline reading from the individual readings.

7.9.2 Treatment of Static Calibration Data

1. Plot the net analyzer readings on the vertical axis versus µl NO_2/ml of the calibrating solutions on the horizontal axis of an appropriate graph paper (rectilinear, semi-log, log, etc). Determine the slope b_s of the static response curve by the method of least squares[c]. To determine the linearity of the response, refer to Test 4.5 in Chapter 4. A non-linear response from an instrument normally linear indicates malfunction in the analyzer or some error in the preparation of the cali-

[c] See Chapter 4, Table 4-V.

brating solutions. Correct the problem(s) before proceeding with the calibration.

2. When a non-linear response is normal, prepare a template as directed in 7.8.6, Step 2. An alternate method is to attempt to linearize the instrument output by adjusting the electronics of the photometer by some combination of photocell voltage and span upperlimit setting until a linear output is found over the concentration range of interest.

7.9.3 Determination of Airflow Rate

1. For instruments not equipped with adjustable upper limit or span controls or when the range of span adjust is insufficient, the slope of the static calibration curve can be used to establish the sample airflow rate that will make the analyzer output correspond to the pollutant concentration or a simple fraction or multiple f_s of the concentration range as follows:

$$Q_a = (Q_r)\,\frac{(f_s)}{(b_s)} \qquad (7)$$

where: Q_a = airflow rate, ml/min

Q_r = reagent flow rate, ml/min

f_s = fraction or multiple of the analyzer range desired

b_s = slope of the static calibration curve obtained in 7.9.2

The NO channel is handled in like manner. Equation 7 is also useful if the analyzer read-out is in $\mu g/m^3$ since the static calibration curve is then units of absorbance versus μg NO_2/ml.

7.10 RECONCILING THE STATIC AND DYNAMIC CALIBRATIONS

The static calibration slope b_s (7.9.2, Step 1) and the dynamic calibration slope b_d (7.8.6, Step 1) are compared by equation 8:

$$R = \frac{|b_s - b_d|}{b_s} \times 100 \qquad (8)$$

Large values of R (≥ 10%) are indicative of a) error in the analyzer's air or reagent flowrate, b) leaks or malfunction in the analyzer, c) poor quality reagents, d) error in the static or dynamic calibration process or e) change in efficiency of collection. Consult the analyzer operating instructions and/or manufacturer and correct the problem(s) before recalibrating.

7.11 REFERENCES

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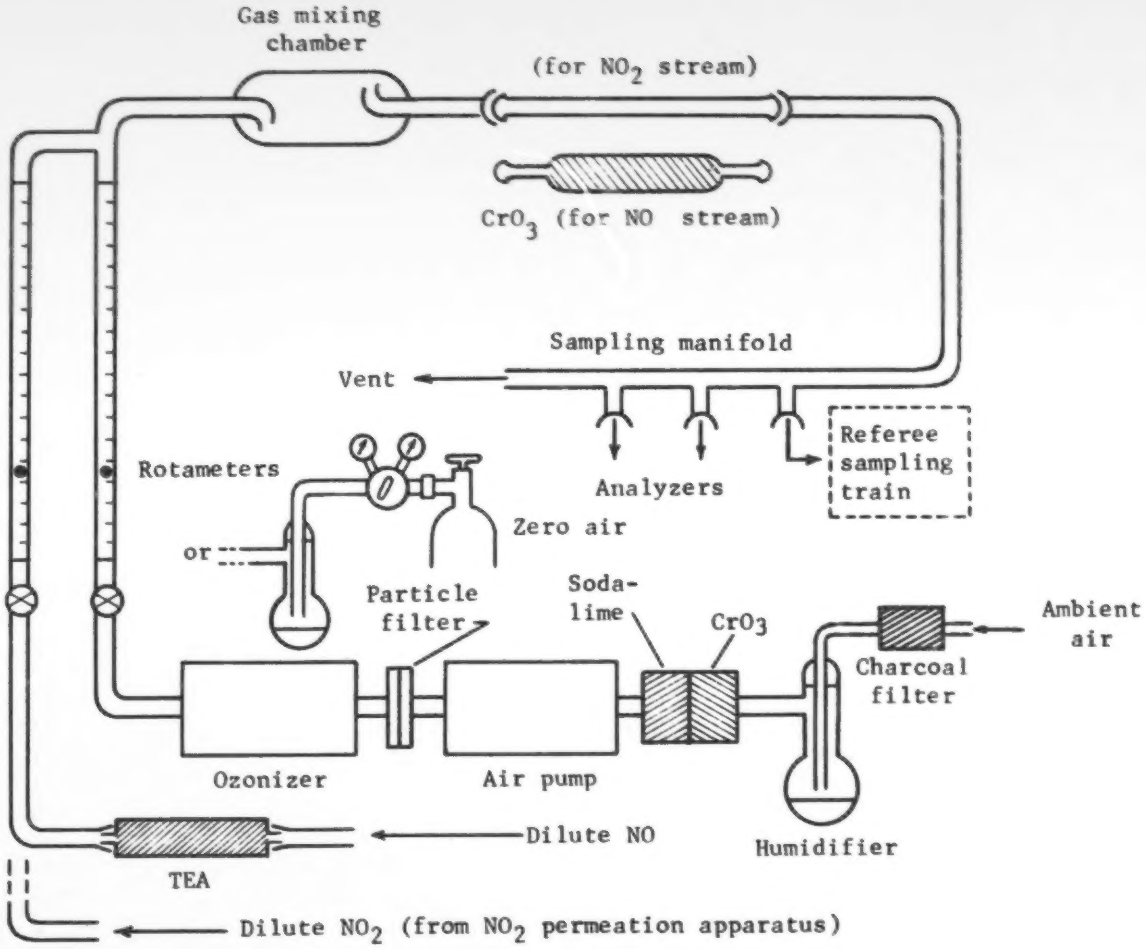
Gas mixing chamber
(for NO_2 stream)
CrO_3 (for NO stream)
Sampling manifold
Vent
Analyzers
Referee sampling train
Rotameters
Zero air
or
Particle filter
Soda-lime
CrO_3
Ambient air
Charcoal filter
Ozonizer
Air pump
Humidifier
Dilute NO
TEA
Dilute NO_2 (from NO_2 permeation apparatus)

Figure 7-1. Gas generating system for calibrating NO and NO_2 analyzers.

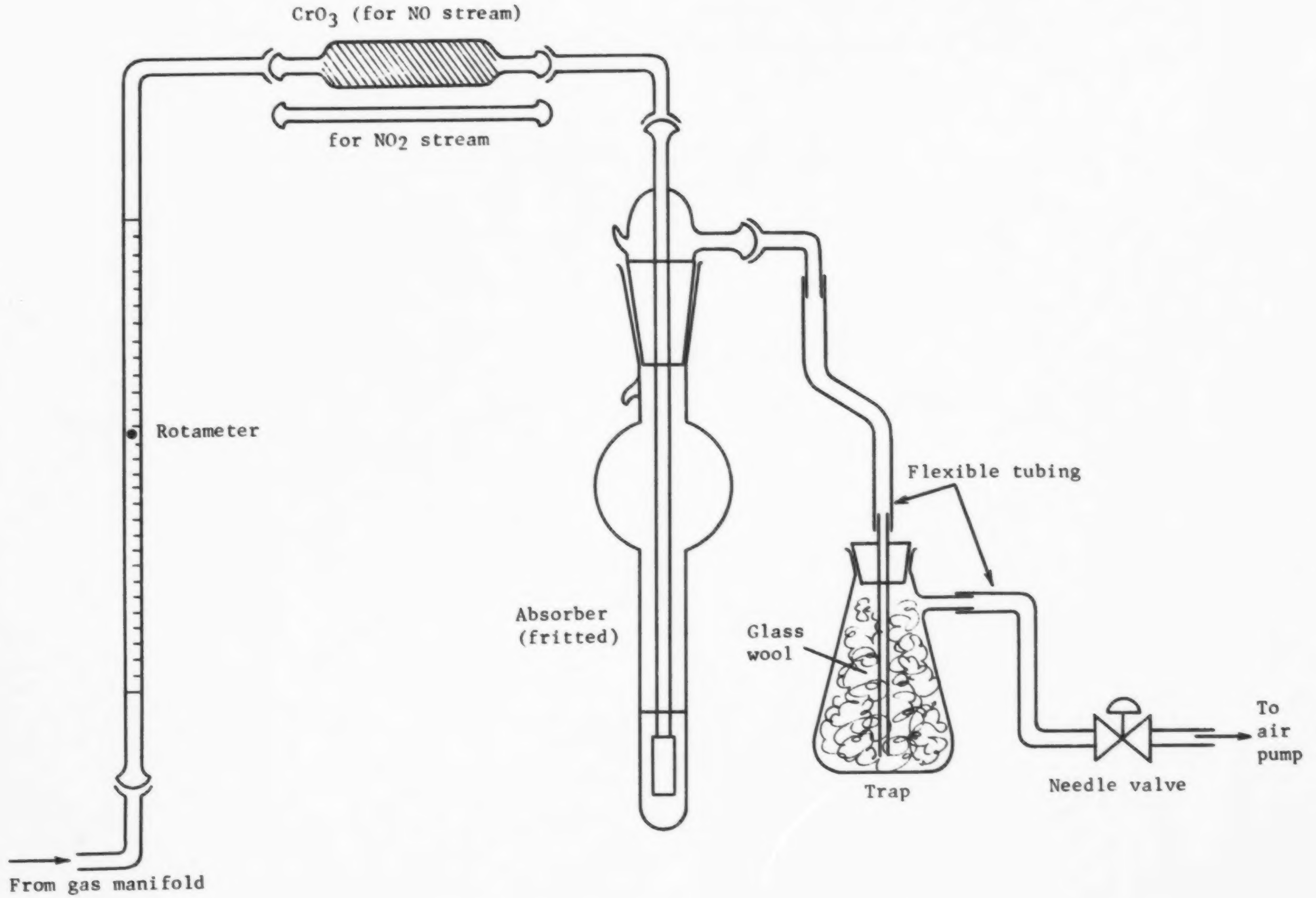
CrO_3 (for NO stream)
for NO_2 stream
Rotameter
From gas manifold
Absorber (fritted)
Flexible tubing
Glass wool
Trap
Needle valve
To air pump

Figure 7-II. Sampling train for referee NO and NO_2 analysis.

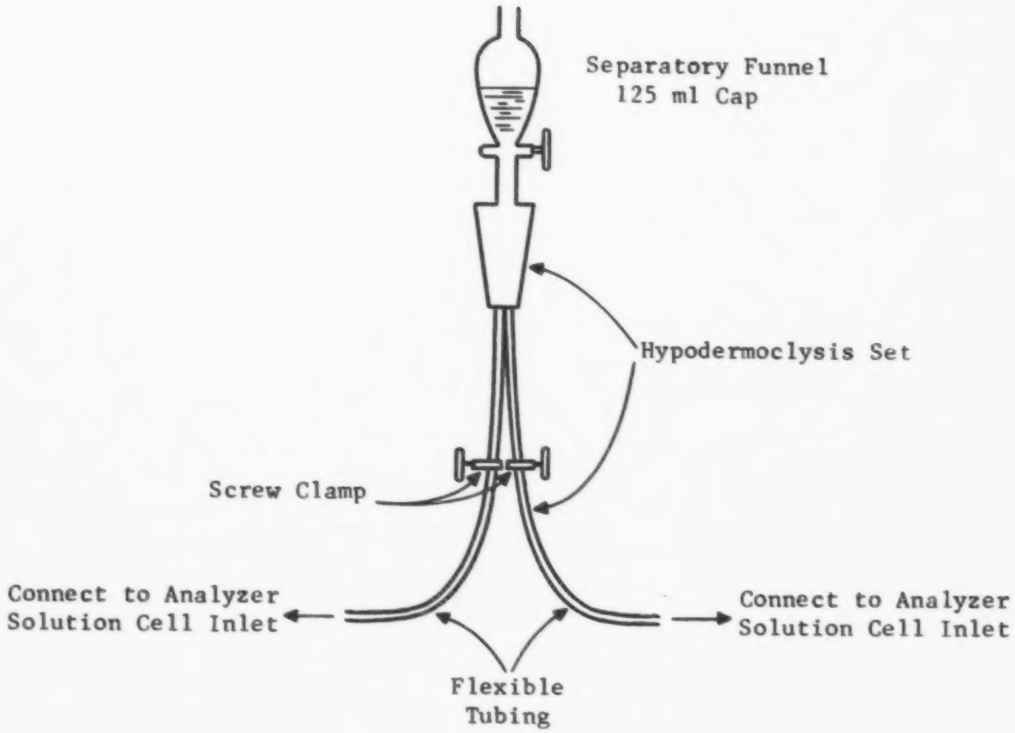
Separatory Funnel
125 ml Cap
Hypodermoclysis Set
Screw Clamp
Connect to Analyzer Solution Cell Inlet
Connect to Analyzer Solution Cell Inlet
Flexible Tubing

Figure 7-III. Calibrating solution dispenser.

8.0 CALIBRATION PROCEDURE FOR AUTOMATED ATMOSPHERIC SULFUR DIOXIDE ANALYZERS

8.1 PRINCIPLE AND SCOPE

8.1.1 This procedure is for the calibration of continuous atmospheric sulfur dioxide analyzers. The calibration may be of two types, dynamic and static. The dynamic calibration must always be done and is performed by determining the analyzer response to a series of sulfur dioxide (SO_2) concentrations. The dynamic calibration is a performance test of the entire analyzer under simulated service conditions and is applicable to all SO_2 analyzers. The static calibration is performed by determining the analyzer response to artificial stimuli such as standard calibrating solutions, optical filters, screens, electrical signals, resistors, etc. This calibration is a test of the detection and signal presentation components only and is primarily applicable to SO_2 analyzers using wet-chemistry such as colorimetry and conductimetry. It is not a substitute for the dynamic calibration.

8.1.2 The calibrating gas for the dynamic calibration may be generated in two ways. The preferred method is by mixing a stream of SO_2 from an SO_2 permeation apparatus[1,2,3] (Figure 8-I) with clean air. Alternatively, streams of dilute SO_2 (50 to 100 ppm; 131 to 262 $\mu g/m^3$) from a cylinder may be mixed with clean air.

The calibrating gas is sampled simultaneously with the analyzer and with the referee method[4] to establish the concentration of the gas. A permeation tube with a known emission rate can be used as a primary standard (see 8.6.1) source of SO_2 gas.

8.1.3 The static calibration is performed by adding known concentrations of a standard reagent to measured volumes of the analyzer absorbing solution which provide an effect equivalent to concentrations of SO_2. These solutions are flowed through the analyzer detector at the actual reagent flow conditions encountered during normal operation. The analyzer readings are plotted versus equivalent SO_2 concentrations to obtain a static calibration curve. The instrument variables, e.g., air and liquid flow rates, may be adjusted to make the output response conform to the pollutant concentration or to a simple multiple or fraction of the concentration in parts per million (ppm) or micrograms per cubic meter ($\mu g\ SO_2/m^3$) (spanning). When a static calibration is not performed, the spanning may be done during dynamic calibration.

8.2 RANGE

The range of the calibration procedure is determined by that of the referee method[4]. For a 10-liter sample collected in 10 ml of absorbing solution and measured in a 1.0 inch cuvette, the range is between 0.01 to 10 ppm SO_2 (0.026 to 26 $\mu g\ SO_2/m^3$).

The measurement range and the sampling rates of continuous SO_2 analyzers vary greatly depending on the detection methods. The upper limit of the measuring range can vary from 0.2 to 10 ppm (0.52 to 26 $\mu g/m^3$). Sampling rates may vary between 0.015 to 5 l/min. A descriptive compilation of most of the currently available SO_2 analyzers is given in Reference 5.

8.3 INTERFERENCES

8.3.1 Interferences are a function of the detection principle as shown in Table 5-IV, Chapter 5. SO_2 with purity greater than 99.9% is readily available. Higher purities are obtainable when required. Zero air for dilution must be free of SO_2 and other substances that can potentially interfere in the analyzer detection principle. Selective absorbers (drying agents, Ascarite for CO_2, etc.) can be used whenever a particular measurement principle requires it. Details for preparing such absorbers are given in Table 5-III, Chapter 5.

8.4 PRECISION, ACCURACY, AND STABILITY

8.4.1 With careful work the coefficient of variation at the 95% confidence level of the pararosaniline referee method is 4.6%[6]. Careful attention to the details of the method is critical.

8.4.2 When spanning is possible, any discrepancy between the input and output may be resolved by adjusting the instrument output to correspond to the calibrating gas concentration. Where analyzers have no spanning controls, a correction factor may be calculated to convert the analyzer readings to SO_2 concentrations.

8.4.3 A detailed discussion of the various sources of error in the preparation of calibrating gases is given in Reference 7, Part I: General Precautions and Techniques. The appreciation and minimization of the sources of errors is important to assure high levels of accuracy and precision.

8.5 APPARATUS

A gas generation system consisting of sources of SO_2 and zero air, flowmeters, gas mixing chamber, sampling manifold and a sampling train for referee analysis is needed in the dynamic calibration (Figure 8-I). The system should be capable of providing calibrating gases between 0.002 to 1.0 ppm (0.005 to 2.6 $\mu g\ SO_2/m^3$). The SO_2 may be furnished from an SO_2 permeation apparatus or from a cylinder of dilute SO_2 gas.

The components and connecting lines making up the system should be sized and assembled so that the differences in the gas pressure between the various components do not exceed 2% overall to prevent errors in flowrate measurements. Ball and socket joints are convenient for connections that are frequently made and broken.

8.5.1 SO$_2$ Permeation Apparatus: See Figure 8-I. This can also be purchased.

1. Flowmeters: To measure the flows of zero air (0 to 1 liter/min) over the permeation tube. They should be calibrated frequently (monthly) with wet or dry test meters, soap bubble meter or calibrated rotameter.

2. Temperature-controlled Bath: Maintained at 20 to 30 ± 0.1°C. It is needed for proper operation of permeation tube 8.6.1. The baths described for SO$_2$[4,7] are acceptable.

3. Needle valves: for controlling the rate of gas flows. Stainless steel type is recommended for SO$_2$.

4. Thermometer: A laboratory type or other temperature-measuring device is needed to measure with a precision of 0.1°C or better the temperature of the constant-temperature bath and the zero air (carrier gas) flowing over the permeation tube.

8.5.2 Gas Dilution Apparatus (when cylinder SO$_2$ is used)

1. Flowmeters: To measure the rate of SO$_2$ and zero air flow. Calibrate frequently (at least monthly) as indicated in 8.5.1, Item 1.

2. Needle Valves: to control gas flow rates. Stainless steel types are recommended for SO$_2$.

3. Mixing Chamber: A cylindrical Kjeldahl type connecting bulb of 200 to 300 ml volume works well. This can also be fabricated from borosilicate glass as shown in Figure 8-I.

4. Sampling Manifold: Fabricate from borosilicate glass (see Figure 8-I). It should contain three or four ports to permit simultaneous sampling of the calibrating gas stream with the analyzer(s) and the referee method.

8.5.3 Zero Air Source

The zero air for diluting the calibrating gas should be free of SO_2 and substances that will in any way 1) change the calibrating gas concentrations, 2) interfere in the analyzer response and 3) interfere in the referee method. The zero air may be furnished from a cylinder or by filtering ambient air as indicated in Figure 8-I.

1. Air pump (for transport of ambient air) - A diaphragm or carbon vane pump capable of delivering flow rate requirements of the total generation system (5 to 10 liters/min) is needed. A particle filter should be installed on the downstream side of carbon vane pumps and is optional for diaphragm pumps.

2. Filters for Ambient Air: See 8.6.4

8.5.4 Manual Sampling Train and Apparatus for Referee Analysis: See Reference 4 and Figure 8-II.

8.5.5 Analytical balance: A laboratory type with a sensitivity of 10 μg or better is needed for weighing the permeation tube.

8.5.6 Calibrating Solution Dispenser (for static calibration): See 7.5.9 and Figure 7-III in Chapter 7.

8.5.7 Apparatus for static calibration: refer to the manufacturer's instructions for a list of the required apparatus.

8.5.8 Absorber (Impingers): See Item 1 in 6.5.4 and Figure 6-III in Chapter 6.

8.6 REAGENTS AND GASES

Purity of chemicals - Unless otherwise specified, all reagent specifications shall conform to the committee on Analytical Reagents of the American Chemical Society[8]. When such reagents are not available, ascertain that they do not lessen the accuracy of the determination.

8.6.1 SO_2 Permeation Tubes: Permeation tubes containing SO_2 are commercially available in a variety of sizes and permeation (emission) rates[9,10]. The rates may be either nominal or certified. Certification can be done by the supplier at additional cost or by the user in his own laboratory. To assure maximum reliability, these tubes should be weighed regularly (e.g., at least once a month) and just before use. Certified tubes can also be obtained from the National Bureau of Standards.

8.6.2 Cylinder SO_2 (50-100 ppm; 131-262 $\mu g/m^3$): This gas mixture is further diluted to produce the desired concentrations for calibration. The concentration produced should never be considered as primary standard and must always be standardized by the referee method or compared to the analyzer response obtained with a certified SO_2 permeation device.

8.6.3 Zero Air: A high-pressure cylinder of synthetic zero air, or filtered ambient air from an air pump may be used.

8.6.4 Zero Air Filter: Activated charcoal and soda lime used together will remove residual SO_2 and most interferents from the zero gas stream. Excessive amounts of nitric oxide in ambient air can be removed by placing a CrO_3 oxidizer (Item 4 in 7.5.1) before the soda lime. Refer to Chapter 7 (calibration method for NO_2 and NO) and Table 5-III for details.

8.6.5 Reagents for Referee Method for SO_2: see References 4 and 7.

8.6.6 Reagents for Static Calibration: refer to the manufacturer's operating instructions for a list of required reagents.

8.7 SPECTROPHOTOMETER CALIBRATION

1. Prepare a series of calibrating solutions containing the equivalent of 0.05 to 0.4 μl SO_2/ml (i.e., 1,2,3 ml) as directed in the manual

referee method[4]. Treat the solutions (Ref 4) and wait 30 minutes for full color development. Determine the absorbance of the solutions on the spectrophotometer against reagent blank.

2. Plot the net absorbances on the vertical axis versus µl SO_2/ml on the horizontal axis of a rectilinear graph paper as a check for linearity. Calculate the slope b of best-fit curve for the data using the method of least squares[a].

8.8 DYNAMIC CALIBRATION

8.8.1 General

1. When a static calibration (8.9) is to be performed on the analyzer, it should be done before the dynamic to assure proper operation of its detection and signal presentation components. The static and dynamic responses may be compared (reconciled) to verify the proper operation of the analyzer and the validity of the calibration. See 8.10 for details.

2. When the analyzer has been operating as a continuous monitor, it is useful to determine its response near the span level first without changing the span settings (auditing). When the response is within ± 10% of the previous calibration, the calibration is still valid and a new calibration is not necessary. When the response is greater than ± 10% proceed with the complete calibration.

[a] See Chapter 4, Table 4-V

The audit data provide a record of the calibration drift. Instruments with non-linear response require the full calibration.

3. The analyzer to be calibrated should be in good operating condition and installed in accordance with manufacturer's instructions. Operate the analyzer for at least 24 hr to warm-up. This 24-hr warm-up period may be shortened if so stated in the operating instructions. Adjust the air and reagent flowrates to their recommended rates or to the rates determined from the static calibration (8.9) data and verify the rates as described in 8.5.1, Item 1.

4. Record all data only after stable analyzer response has been attained. Refer to 4.1.6 in Chapter 4 for determining stable response.

5. Newly prepared SO_2 permeation tubes may be used after one day (24 hr) of equilibration at a constant temperature provided the concentrations produced are established by the referee method. A minimum of 30 days is required to establish that the emission rate is stable and before the emitted concentration can be used as a primary standard[1]. The tube should be equilibrated for at least 12 and preferably 24 hours whenever the temperature is changed by more than ± 5°C. See Reference 7 for general precautions pertaining to permeation tubes. It is generally desirable

to precondition all SO_2 gas lines for ½ to 1 hour by flowing a stream of dilute SO_2 through them.

8.8.2 Procedure

1. Place the gas generation system as close as practical to the analyzer to prevent losses and to minimize pressure changes in the analyzer sampling duct. Calculate the airflow of the analyzer and add the airflow needed for the referee analysis (1.0 to 2.0 liter/min). Add about 10% of the total to insure an excess. (NOTE: The excess calibrating gas should be vented to a hood or absorbed by a soda lime trap to avoid exposure to personnel.) In a proper assembly, connection or disconnection of the analyzer sampling line should not alter the airflow settings.

2. Generate a flow of zero air equal to the rate determined in Step 1 above. Pipet the required volume of absorbing reagent in the impinger (Item 8.5.8) according to the manual referee method[4]. Connect the impinger to the sampling train as shown in Figure 8-III. When a stable analyzer response is obtained, sample the gas stream from the manifold for 30 minutes at the rate directed in Reference 4. Transfer the exposed solution to a 25 ml volumetric flask. Develop the color of the solution in accordance with the referee procedure[4] and read the absorbance at 560 nm. When the absorbance of the solution is greater than the blank, continue flushing the gas generation system until the absorbance is obtained the same as the blank. Inability to

obtain a reading equal to the blank indicates interferents in the zero air. Correct the source of the problem(s) before proceeding.

Zero the analyzer by adjusting the analyzer controls so that the output corresponds to zero or the desired reading.

3. Generate an SO_2 concentration equal to 80 ± 5% (span gas) of the full scale reading (0.80 ppm for full scale of 1.0 ppm; 2.10 $\mu g\ SO_2/m^3$ for full scale of 2.62 $\mu g/m^3$). When the analyzer response is steady, record the analyzer reading.

4. When a permeation tube system is used and has been shown by frequent referee analysis to provide reliable SO_2 concentrations, the collection of referee samples may be omitted. The SO_2 concentrations are calculated from the diluent gas flow and permeation rates by equation 1 or 2.

   a) To determine the concentration of SO_2 in ppm ($\mu l/l$) from the permeation tube emission rate, use equation 1.

$$\text{ppm} = \frac{P}{2.62\ (Q_d)} \qquad (1)$$

where P = permeation rate in μg/min.

Q_d = rate of zero (diluent) air in liters/min.

b) When the concentration units are desired in $\mu g\ SO_2/m^3$ instead of ppm, then:

$$\mu g\ SO_2/m^3 = \frac{(R \times 10^3)\ (\ell/m^3)}{(Q_d)} \qquad (2)$$

5. To establish the SO_2 concentration by referee analysis:

a) Collect duplicate samples of the gas stream and analyze as described in the referee method[4]. Adjust the sampling period to keep the absorbances of the samples at about midscale (0.3 to 0.5A) on the spectrophotometer. Five to 30 minutes are usually sufficient. For maximum precision, place the flasks containing the reacted solutions in a bath maintained within 2°C of the temperature used during the development of the spectrophotometer calibrating solutions.

b) From the volume of air sampled and the slope of the spectrophotometer calibration curve, calculate the ppm SO_2 as directed in equation 3.

$$\text{ppm} = \frac{(A)\ (10)}{(b)\ (V_a)} \qquad (3)$$

where: ppm = concentration ($\mu l/l$) SO_2

A = net absorbance of the solution

b = slope of the spectrophotometer calibration curve obtained in 8.7

V_a = volume, in liters, of the gas sample collected (liters/min X min)

To convert ppm to $\mu g/m^3$, use equation 4

$$\mu g\ SO_2/m^3 = ppm\ SO_2 \times 2620 \qquad (4)$$

Usually, changes in the gas volume of the samples due to deviation from the standard conditions of 25°C and 760 torr are small and may be neglected. When the deviations are large, (sufficient to cause a change in gas volume greater than about 5%) correction should be made.

c) The concentrations of the duplicate samples should be within 5%. Differences greater than 5% may be due to unstable gas concentrations, error or inconsistencies in sample collection and analysis. Correct these problems before proceeding with the calibration.

6. When possible, adjust the analyzer to give reading equivalent to the span SO_2 concentration (spanning). When the instrument has no span controls, proceed to Step 7 below. Generate zero air and note the analyzer reading. When the reading is different from the original baseline reading by ≥ 2%, reset the analyzer to read the original baseline and repeat Steps 3 through 6 above. Analyzers with zero and span controls not electrically independent may have to be respanned and rezeroed iteratively until the proper zero and span settings are obtained.

7. Generate, in turn, four additional SO_2 concentrations between the blank and span range (e.g., 10, 20, 40, and 60% of full scale) and determine the SO_2 concentrations in duplicate and analyze as directed in Steps 3 through 5 above. Determine the net analyzer readings by subtracting the baseline reading from the individual readings.

8.8.3 Treatment of Dynamic Calibration Data

1. Plot the net analyzer readings on the vertical axis versus the corresponding SO_2 concentrations on the horizontal axis of an appropriate graph paper (rectilinear, semi-log, log, etc.). Calculate the slope b_d of the best-fit curve for the data by the method of least squares[b]. To determine the linearity of the response, see Test 4.5 in Chapter 4. A non-linear response from an instrument normally linear indicates analyzer malfunction or, possibly, errors in the preparation of the calibrating gases. Correct the cause of the problem(s) before recalibrating.

2. When a non-linear response is normal, draw a smooth line through the calibration points that fits the points best. From this, prepare a template to convert the net analyzer readings to SO_2 concentrations.

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[b] See Chapter 4, Table 4-V.

8.9 STATIC CALIBRATION

The following section pertains to SO_2 analyzers using wet-chemical methods (colorimetry and conductimetry). See also 8.1.3.

8.9.1 Procedure

Prepare calibrating solutions (equivalent to 10, 20, 40, 60, and 80% of full scale and perform the static calibration according to manufacturer's instructions. In the absence of such instructions the static calibration procedures described in Section 6.9, Chapter 6, for automated oxidants and ozone analyzers may be used as a guide.

8.9.2 Treatment of Static Calibration Data

1. Plot the net analyzer readings on an appropriate graph paper (rectilinear, semi-log, etc.) against the equivalent µl SO_2/ml of the calibrating solutions. Calculate the slope b_s of curve that best-fits the data by the method of least squares[c]. To determine the linearity of the response, see Test 4.5 in Chapter 4. A non-linear response from an instrument normally linear indicates malfunction in the analyzer or error in the static calibration process. Correct problem(s) before recalibrating.

2. When a non-linear response is normal, prepare a template as directed in Step 2 of 8.8.3. An alternate method is to

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[c] See Chapter 4, Table 4-V.

attempt to linearize the instrument output by adjusting the electronics (i.e. photometer, etc.) until a linear output is found over the range of pollutant concentration of interest.

8.9.3 Determination of Airflow Rate

For instruments not equipped with adjustable upper limit or span controls or when the range of span adjust is insufficient, the slope of the static calibration can be used to establish the sample airflow rate that will make the analyzer output correspond to the pollutant concentration or a simple fraction or multiple f_s of the concentration range as follows:

$$Q_a = (Q_r) \frac{(f_s)}{(b_s)} \qquad (5)$$

where: b_s = slope of the static calibration curve obtained in 8.9.2

Q_a = analyzer airflow rate, ml/min.

Q_r = analyzer reagent flow rate, ml/min.

f_s = range factor (e.g., ½, 1.0, 2.0)

8.10 RECONCILING THE STATIC AND DYNAMIC CALIBRATIONS

The static calibration slope b_s (8.9.2) and the dynamic calibration slope b_d (8.8.3) are compared by equation 6:

$$R = \frac{|b_s - b_d|}{b_s} \times 100 \qquad (6)$$

Large values of R ($\geq$ 10%) are indicative of a) error in the analyzer's air or reagent flowrate, b) leaks or malfunction in the analyzer c) poor quality reagents, d) error in the static or dynamic calibration process or e) change in the sample collection efficiency of the analyzer. Consult the analyzer operating instructions and/or manufacturer and correct the problem(s) before recalibrating.

8.11 REFERENCES

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9. Metronics Associates, Inc., Palo Alto, CA 94304.

10. Analytical Instrument Development, Inc., 250 South Franklin Street, Westchester, PA 19380.

11. National Bureau of Standards, Office of Standard Reference Materials, Washington, DC 20234.

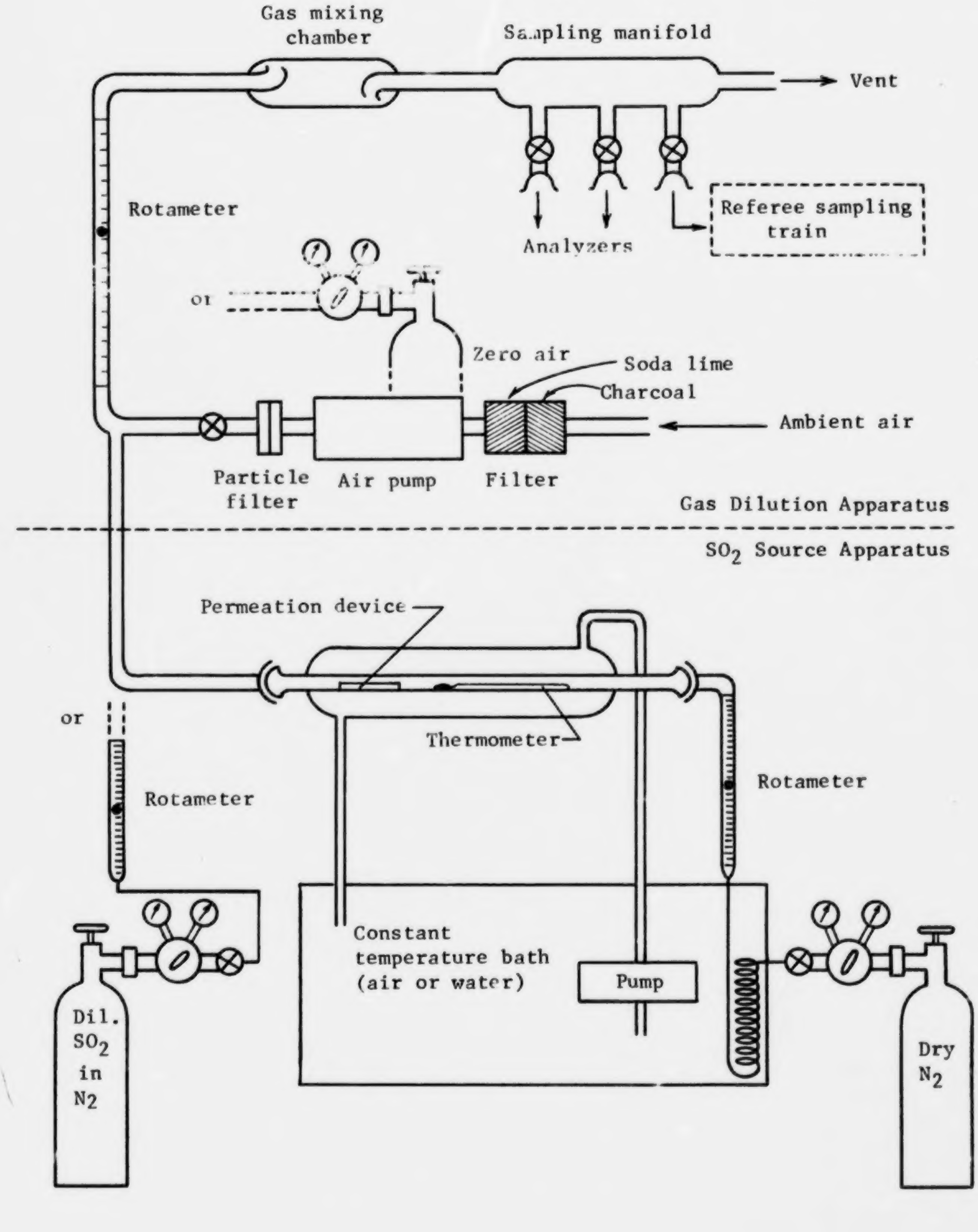
Gas mixing chamber
Sampling manifold
Vent
Rotameter
Analyzers
Referee sampling train
or
Zero air
Soda lime
Charcoal
Ambient air
Particle filter
Air pump
Filter
Gas Dilution Apparatus
SO_2 Source Apparatus
Permeation device
or
Thermometer
Rotameter
Rotameter
Constant temperature bath (air or water)
Pump
Dil. SO_2 in N_2
Dry N_2

Figure 8-1. Gas generating system for calibrating SO_2 analyzers.

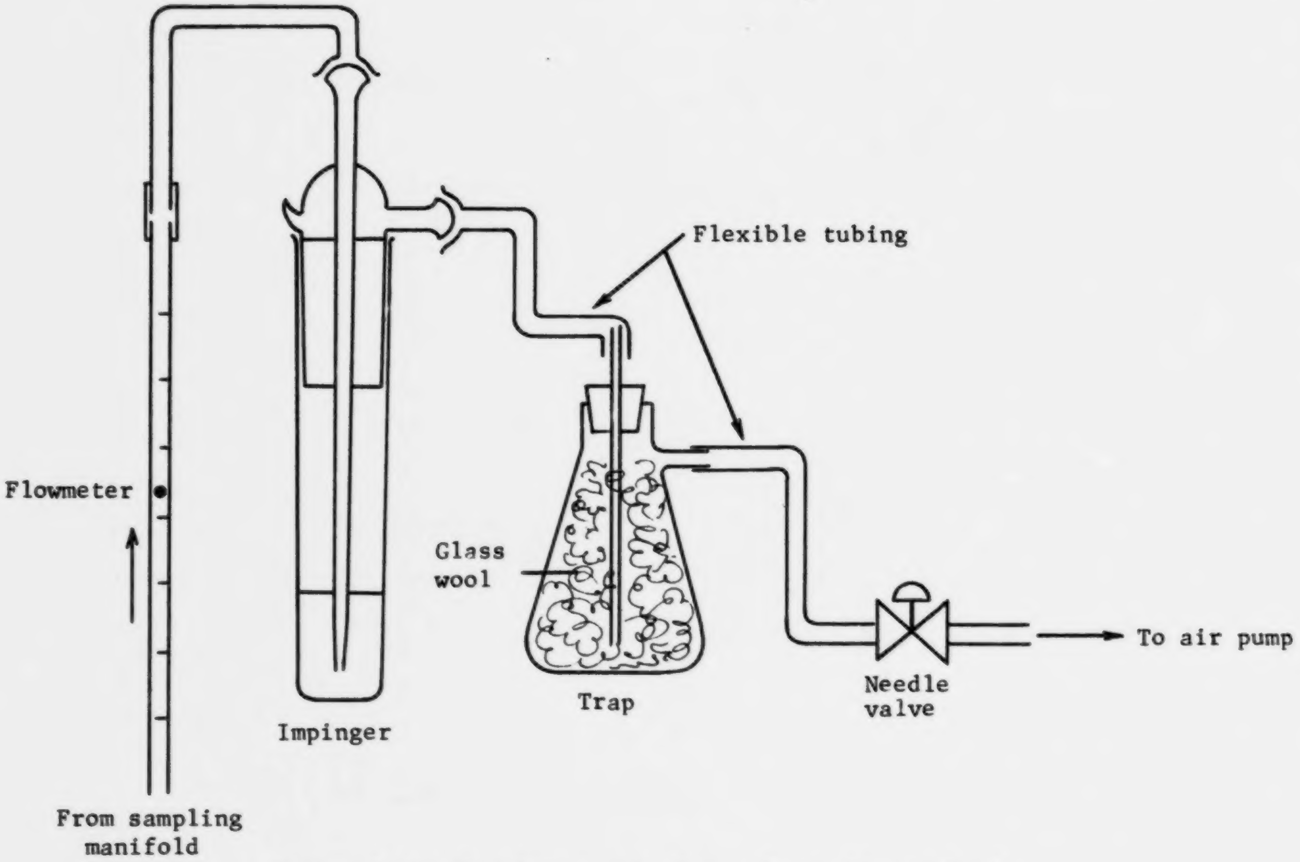
Flexible tubing
Flowmeter
Glass wool
Impinger
Trap
Needle valve
To air pump
From sampling manifold

Figure 8-II. Sampling train for referee SO_2 analysis.

9.0 CALIBRATION PROCEDURE FOR AUTOMATED ATMOSPHERIC CARBON MONOXIDE ANALYZERS

9.1 PRINCIPLE AND SCOPE

9.1.1 This procedure is for the calibration of continuous atmospheric carbon monoxide (CO) analyzers that use physical measurement methods such as nondispersive infrared absorption, etc. The calibration, known as a dynamic calibration, is performed by determining the analyzer response to a series of calibrating gas concentrations containing CO. It is a performance test of the entire analyzer under simulated service conditions.

9.1.2 The calibrating gas concentrations may be generated in several ways[1,2]. The most common method is to prepare a series of CO concentrations in plastic bags (primary or batch dilution) or to prepare or purchase cylinders of compressed air containing CO concentrations between 10 to 80% of full scale (primary standard). A wider variety of concentrations may be generated by diluting 50 to 100 ppm (57 to 115 mg/m^3) CO from a cylinder with zero air (secondary dilution).

9.1.3 The instrument operating variables, such as airflow rates, output, gain, span, can be adjusted during calibration to make the output reading conform directly to concentration in ppm (μl/1) or mg CO/m^3 or a simple fraction or multiple of the concentration.

9.2 RANGE

The range of the calibration procedure depends on the measuring range(s) and sampling rate(s) of the analyzer(s). The analyzer's measuring range and sampling rates vary greatly depending on its design and measurement principle (See Reference 2 and its lists of references for further details). The commonly used nondispersive infrared (NDIR) analyzers typically measure in the range of about 0 to 25, 50, or 100 ppm CO (0 to 28.6, 57.3, or 115 mg CO/m^3). Sampling rates are typically between 1 to 2 l/min, but can go as high as 42 l/minute (See Table 5-I). The semi-continuous gas-chromatographic CO and methane analyzers measure CO concentrations between 0 to 1000 ppm (0 to 1145 mg/m^3). Electrochemical analyzers measure in the same range although they are not much used for continuous ambient monitoring.

9.3 INTERFERENCES

Carbon monoxide is available with purities of 99.7% or greater. Higher purities are obtainable for special work. Zero air for dilution must be free of CO, CO_2 and water. Selective absorbers (drying agents, Ascarite for CO_2, etc.) can be used whenever a particular measurement principle requires it. Details for preparing these absorbers are given in Table 5-III.

9.4 PRECISION, ACCURACY, AND STABILITY

9.4.1 A precision (coefficient of variation) from 2 to 3% is achievable when preparing repeated primary dilutions of CO in non-rigid, CO-inert bags in the range of 10 to 100 ppm (12 to 115 mg/m^3). The chief source of error is often in measuring the air volumes. A minimum of 2% error is produced for each rotameter used and the errors are approximately additive. When greater precision is needed, positive displacement, metering pumps can be used.

9.4.2 When spanning is possible, any discrepancy between the input and analyzer output may be resolved by adjusting the instrument output to correspond to the concentration of the calibrating gas. Where analyzers have no spanning controls, a correction factor may be calculated to convert the analyzer readings to CO concentrations.

9.4.3 Primary dilutions made in non-rigid containers usually cannot be kept for more than a few (< 5) days due to concentration changes with time. The concentration of dilute CO (> 50 ppm) stored at high pressure in steel cylinders lined with chromium molybdenum alloy should be checked periodically (∿ monthly) for one to three months after preparation and semi-annually thereafter. See 9.6.2 for additional comments.

A detailed discussion of the various sources of error in the preparation of calibrating gases is given in Reference 1 in

Part I: General Precautions and Techniques. The minimization of the sources of error is important to assure high accuracy and precision in calibration.

9.5 APPARATUS

The apparatus needed depends on the method chosen. The procedures listed under 9.7 are the easiest as well as among the most reliable. For delivering large (> 40/min) flows, procedure 9.7.3 is preferable. The fourth, indicated in 9.5.4 and discussed in Reference 1, is less commonly used, although equally reliable. The zero air may be furnished from a cylinder or by filtering ambient air as shown in Figure 9-I.

9.5.1 Primary Standards

Refer to 9.6.2 for equipment and gases.

9.5.2 Primary Dilution in Bags

1. Bags: (Scotchpak[a]): Fabricate or purchase six bags of sufficient volume (10 to 20 l) to satisfy the volume rate requirement of the analyzer. Use one bag for each gas concentration.

2. Dilution system (Figure 9-I): consists of a flowmeter for measuring gas flows between 1 to 5 liters/min, a needle valve,

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[a] Registered trademark of Minnesota Mining & Manufacturing Co. (3M) for their metallized laminate consisting of polyester, aluminum, and polyethylene, Cat. No. 20A20.

a three-way stopcock for diverting flows, a tee connection with a rubber septum cap for injection of known volumes of pure CO and the necessary glassware and ball-and-socket joints. Polyvinylchloride tubing may be used to butt-join connections.

The rotameter should be calibrated frequently (monthly) with a wet or dry test meter, soap bubble meter or calibrated rotameter.

3. Gas Sampling syringes[b]: A 1.00 ml syringe is needed for preparing the CO concentrations in bags.

4. Stopwatch or accurate timing device.

9.5.3 Secondary Dilution of Cylinder CO

1. Dilution system (Figure 9-II): This consists of a mixing chamber, two flowmeters capable of measuring the maximum flow required by the analyzer(s), two needle valves for flow control and a delivery manifold containing sampling ports and a vent for discharging excess calibrating gas and the necessary glassware and ball-and-socket joints. Rotameters should be calibrated frequently (monthly) with a wet or dry test meter, soap bubble meter or calibrated rotameter.

[b] Precision Sampling Corp., Baton Rouge, LA, Series A, or equivalent.

2. Air pump (for transport of ambient air): An oil-less (carbon vane or diaphragm) air pump capable of delivering the flow rate requirements of the total calibration system plus 10%. A particle filter should be installed downstream of carbon vane pumps and is optional for diaphragm types.

9.5.4 CO in Cylinders (Low Pressure): See Reference 1 for apparatus and method.

9.6 REAGENTS AND GASES

9.6.1 100% Carbon Monoxide, Chem. Pure (> 99.7%): For preparing CO in bags by Method 9.7.2, Primary Dilution.

9.6.2 Dilute Carbon Monoxide (Primary Standards): High pressure steel cylinders containing CO concentrations equal to 10, 20, 40, 60 and 80 ± 5% of full scale in air. Cylinders should be lined with a chromium molybdenum alloy. Alternatively, the 80% of full scale cylinder may be used for spanning and for preparing intermediate concentrations by Method 9.7.3 (Secondary Dilution). These mixtures may be purchased or may be prepared in the laboratory with suitable gases and high-pressure manifold[3]. The CO concentrations are established by comparing the analyzer readings obtained with this gas versus those obtained with 1) a primary dilution, 2) certified CO gas from another source, or 3) analyzed gravimetrically[1,2]. Certification or analysis by the supplier at the time of preparation is of little value because of unpredictable changes that frequently occur with time. Verify the concentration monthly for one to three months after purchase or preparation, and occasionally (semi-annually) thereafter. NOTE: Since changes in the CO concentration may occur after the cylinder pressure depletes to between 200 to 500 psig (138 to 345 Newton/cm^2), it is desirable to again verify the concentration more frequently (monthly) or preferably the cylinder should be refilled (See also Chapter 5, 5.2.4, for further discussion).

9.6.3 Zero Air Source: The zero air for zeroing the analyzer and diluting the calibrating gas should contain less than 0.1 ppm CO (∿ 0.1 mg/m^3) and be free of any substances that will in any way a) change the CO gas concentration, b) interfere in the analyzer response or c) interfere in the referee procedure. A high-pressure cylinder of compressed synthetic air, or filtered ambient air coupled to an air pump may be used. A Hopcalite CO-to-CO_2 converter followed by a tube of soda lime or Ascarite can be used to remove any CO. Other filtering aids (drying agents or activated carbon) may be added to remove other interfering compounds from the ambient air stream. Refer to Table 5-III in Chapter 5 for details.

9.6.4 Reagents for gravimetric determination of CO (optional): See Reference 1. NOTE: The time for sample collection by this method is 2 to 4 hours.

9.7 PREPARATION OF CALIBRATING GASES

9.7.1 Primary Standards

Equip the zero air cylinder (Item 9.6.3) and each CO cylinder (Item 9.6.2) with an appropriate pressure reducing regulator, metering valve and flowmeter. These gases may be fed directly to the analyzer.

9.7.2 Primary or Batch Dilution in Bags

1. Assemble the dilution system described in Item 2 of 9.5.2 and shown in Figure 9-I. Generate a convenient flow of zero air (i.e., 1000 ml/min). From the volume of the bag, calculate the volume of pure CO (Item 9.6.1) needed to prepare the desired CO concentration by equation 1. The volume of diluent zero air depends on the size of the bag and should not exceed about 80% of the bag volume.

$$V_o = 1 \times 10^{-6} (V_1) (C_1) \qquad (1)$$

where: V_o = volume of pure CO in ml

C_1 = ppm CO desired

V_1 = volume of zero air and CO added to the bag in ml.

To convert ppm CO to mg CO/m^3:

$$\text{mg CO/m}^3 = (1.15)\ (\text{ppm CO}) \qquad (2)$$

Usually, the change in gas volumes due to deviation from the standard conditions of 25°C and 760 torr is small and may be neglected. When the deviations are large (sufficient to cause a change $\geq$ 5% in gas volume), volume corrections should be made.

2. Connect the bag (with its valve open) to the three-way stopcock. Carefully fill the gas-tight syringe to the calculated volume V_o with pure CO. Switch the stopcock to fill the bag with zero air and begin timing. Insert the syringe needle through the rubber septum cap on the glass tee and expel the pure CO so that it merges with the zero air stream. Continue filling the bag until the predetermined volume V_1 is reached, then switch the three-way stopcock to vent. Seal the valve on the bag and knead the bag to mix the gases thoroughly. Empty the contents to a hood and repeat Step 2 twice. Prepare the four other intermediate CO concentrations in the same manner. These primary dilutions may be prepared in duplicate or larger multiples and the analyzer responses averaged to insure against errors or to acquire precision data.

9.7.3 Secondary Dilution

1. Assemble the dilution system (Item 1 of 9.5.3) as shown in Figure 9-II. Connect the cylinder of dilute CO (Item 9.6.2) and the zero air source (Item 9.6.3) to the needle valves of their respective rotameters.

9.8 DYNAMIC CALIBRATION

9.8.1 General

1. When the analyzer to be calibrated has been operating as a continuous monitor it is useful to determine its response near the span level first without changing the span setting (auditing). When the analyzer response is within ± 10% of the previous calibration, the calibration is still valid and a new calibration is not needed. When the response is greater than ± 10% proceed with the complete calibration. The audit data provide a record of the calibration drift. Instruments with non-linear response requires the full calibration.

2. The instrument to be calibrated should be in good operating condition and installed in accordance with manufacturer's instructions. Operate the analyzer for at least 24 hours to warm-up. This 24-hr warm-up period may be shortened if so stated in the operating instructions. Adjust the analyzer

airflow to the recommended sampling rate and verify the rate as described in 9.5.2, Item 2.

3. Record all data only after stable analyzer response has been attained. Refer to 4.1.6 in Chapter 4 for determining stable response.

4. Assemble the appropriate generating system (Items 9.5.1, 9.5.2 or 9.5.3)for generating CO as needed. Place the system as close as practical to the analyzer to prevent losses and to minimize pressure changes in the analyzer sampling duct. Calculate the airflow of the analyzer and, when required, add the airflow needed for the referee analysis. Add 10% of the total to insure an excess. (NOTE: Any excess CO gas streams should be vented or passed through a CO oxidizer/CO_2 absorber filter to avoid exposure to personnel. See Table 5-III for details.) In a proper assembly, connection or disconnection of the analyzer sampling line should not alter its airflow reading.

5. Generate a flow of zero air equal to the rate determined in Step 4 above. When a stable analyzer reading is obtained, adjust the analyzer zero control so that the analyzer output reads zero or the desired baseline reading.

6. Generate a flow of calibrating CO gas equal to 80 ± 5% of full scale (span gas). When a stable response is obtained, adjust

the analyzer controls to give a reading equivalent to the span CO concentration. Generate a zero gas. When the zero reading is different from the original baseline reading by ≥ 2%, reset the analyzer to read the original baseline and repeat Steps 5 and 6. When the span and zero controls are not electrically independent, it may be necessary to rezero and respan iteratively until the proper zero and span control settings are obtained.

7. In turn, generate and introduce the four intermediate CO concentrations (e.g., 10, 20, 40 and 60% of full scale) from the bags or from the dilution system and record the corresponding instrument readings. Determine the net analyzer readings by subtracting the baseline reading from the individual readings.

9.8.2 Treatment of Dynamic Calibration Data

1. Plot the net analyzer readings on the vertical axis versus the CO concentrations on the horizontal axis of an appropriate graph paper. Calculate the slope b of the best-fit curve for the data by the method of least squares[c]. To determine the linearity of the response, see Test 4.5 in Chapter 4. A non-linear response from an instrument normally linear indicates

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[c] See Chapter 4, Table 4-V.

malfunction or, possibly, errors in the concentrations of the calibrating gas. Correct the problem(s) and recalibrate.

2. When a non-linear response is normal, draw a smooth line through the calibration points that fits the data best. From this, prepare a template to transform the net analyzer readings to CO concentrations.

9.9 REFERENCES

1. Intersociety Committee: Methods of Air Sampling and Analysis. Tentative Method of Preparation of Carbon Monoxide Standard Mixtures, No. 117, Amer Publ Hlth Assn, Wash., DC (1972).

2. U.S. Dept. of Health, Ed. & Welfare, Publ. Hlth Serv., Envir. Hlth Serv.: Air Quality Criteria for Carbon Monoxide, Ch. 5, NAPCA Publ. No. AP-62 (March 1970).

3. Belsky T: Preparation of low-concentration mixtures of gases. Air & Industrial Hygiene Lab., Cal. State Dept. of Publ. Hlth, AIHL Report No. 117 (Jan. 1972).

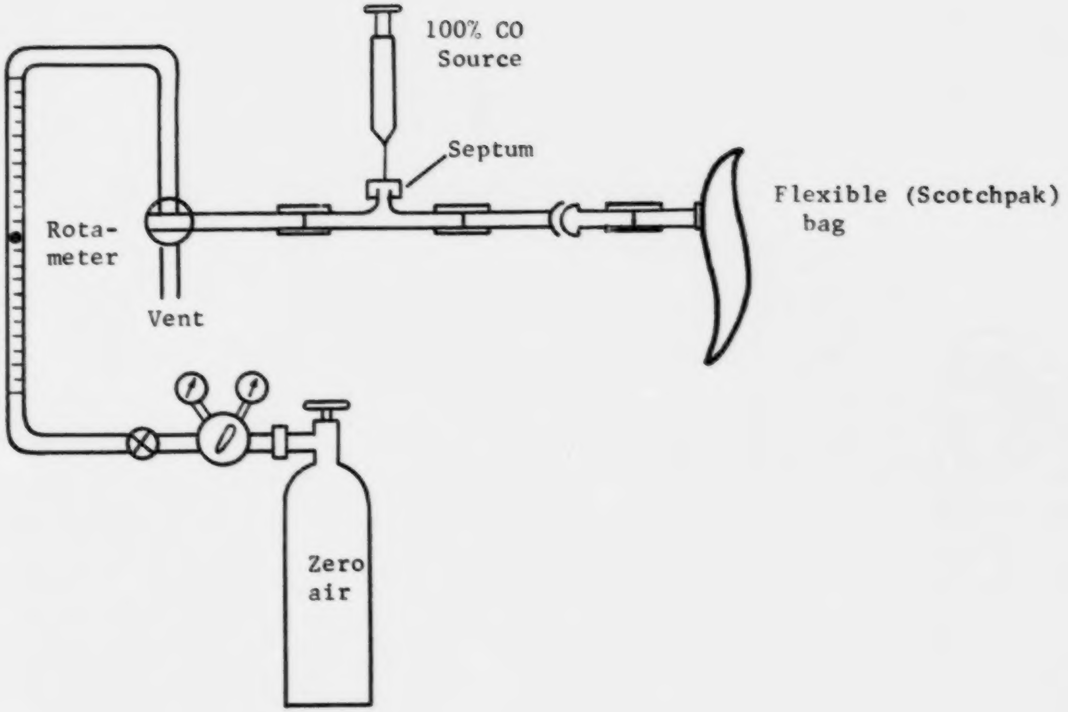

100% CO
Source
Septum
Flexible (Scotchpak)
bag
Rota-
meter
Vent
Zero
air

Figure 9-1. Primary dilution system for CO in bags.

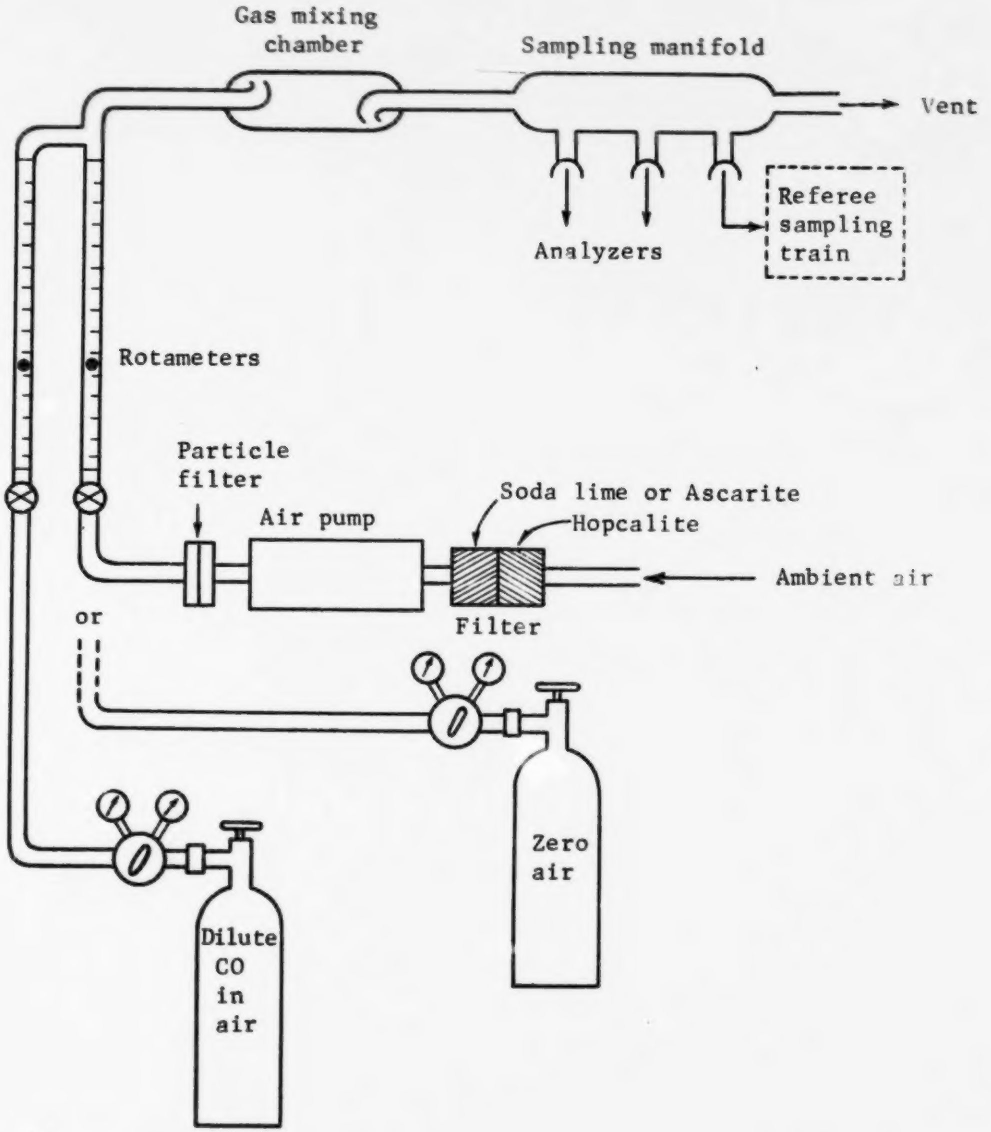

Gas mixing chamber
Sampling manifold
Vent
Analyzers
Referee sampling train
Rotameters
Particle filter
Air pump
Soda lime or Ascarite
Hopcalite
Ambient air
Filter
or
Zero air
Dilute CO in air

Figure 9-11. Secondary dilution system for calibrating CO analyzers.

10.0 AIR ANALYZER TERMINOLOGY

This chapter contains selected terms commonly used in air monitoring practices and instrumentation and was developed to promote more effective communication between the various disciplines in air pollution technology. It is not intended as an all-inclusive glossary of air pollution terms.

The emphasis of terms related to instrument performance applies to the overall analyzer system and not to the individual components.

For visual representation and interpretation of noise and of the various time delays in instrument response, see Figure 10-I.

Absorbent: a medium, which absorbs the pollutant being measured.

Absorber (contactor, contact column, scrubber): a device for bringing a gas stream containing vapors, fumes or particulate matter into intimate contact with a liquid absorbent usually aqueous. To minimize absorption of interferents, an absorber design with minimum turbulence and minimum surface area consistent with absorption of the pollutant is desirable.

Bubbler: an absorber in which the sample gas is introduced below the surface of a liquid absorbent. For increased efficiency, the gas stream may be broken up into small bubbles by being forced through restricted openings as in a perforated sparger or a fritted glass tip. Bubblers may be tall or short depending on the efficiency of the absorbing process.

Helical column: an absorber consisting of a coil of tubing with one or more turns, usually mounted with its axis vertical. Gas-liquid flow is co-current and may be up or down the column. High wetted-surface area is achieved by selecting a tube diameter sufficiently small to insure that the surface tension of the absorbent will cause the entire inner surface of the column to become wetted. The coil is usually glass, but other materials may be used.

Helix insert column: a high-surface-area absorber composed of a narrow vertical tube with a solid helix, usually of glass or wire, placed axially and in contact with the interior column wall. Liquid absorber passes down the column in a thin film over the helix. Gas-liquid flow may be co-current or countercurrent. The helix may also be wrapped around a center support with the gas-liquid mixture passing between it and the column wall.

Impinger: an absorber in which sample air is blown or aspirated onto or below the surface of the liquid absorbent. Absorption is increased by both high surface area and by turbulence.

Mechanical absorber: an absorber designed to bring a gas or gases and liquid absorbent into intimate contact by mechanical agitation. Absorption is increased by both high surface area and by turbulence.

Packed column: a high-surface-area type absorber, usually a vertical tubular column loosely filled with an inert medium such as Raschig rings, helices, crushed or sintered glass, beads or other materials of various shapes. Gas and liquid flow may be co-current or countercurrent with absorption taking place on wetted surfaces. A single or a series of sintered glass plates through which the gas-liquid mixture is passed may be used in place of inert packing.

Spray jet: an absorber in which a liquid absorbent is forced through an orifice at high velocity and impacted on the inner surface of the absorbing chamber. Gas is absorbed through mixing and turbulence created by the impaction. Kinetic energy is imparted to the liquid by hydraulic pressure, sample air pressure, or by aspiration caused by the airflow into the chamber.

Absorption: a process in which one or more pollutants are transferred from a gas phase to a liquid or solid phase, either by physical dissolution in, or preferably by chemical reaction with the absorbent. The driving force is a function of the pollutant partial pressure at the gas-absorbent interface. The process is favored by high interfacial areas, turbulence, and high diffusion coefficients and, where the absorption process is chemical, fast reaction rates and irreversible reactions.

Absorption spectroscopy: see detection methods.

Accuracy: (not to be confused with precision) the deviation between the analyzer output in concentration units and true pollutant concentration which has been established by an accepted reference procedure. It is expressed as a percent of the true concentration.

Accuracy, calibration: deviation between the slope b_m of the curve obtained by the manufacturer's calibration procedure and slope obtained with calibrating gases expressed as a percent of the manufacturer's slope.

Accuracy, monitoring: deviation between the analyzer response obtained under actual monitoring conditions to that of a reference procedure when samples of the same atmosphere are taken at approximately the same time. It is expressed as a percent of the reference procedure.

Adsorption: a process in which one or more pollutants are transferred from a fluid to a solid by physical binding to the surface of the solid. Adsorption is usually reversible, the pollutant being released (desorbed) by methods such as solvent elution, evacuation, or heating.

Amperometry: see detection methods.

Analyzer (also monitor): a device or an instrument for sampling and assaying pollutants.

Analyzer deadband: see deadband, analyzer.

Anemometer: an instrument for measuring and indicating wind speed.

Audible noise (also acoustical noise): 1) any unwanted sound, 2) an erratic, intermittent or statistically random acoustical oscillation; commonly expressed in units of power (decibels) sound pressure (newton or dyne/square area) or loudness (phones, sones, noys).

Auxiliary equipment: accessory items designed but not normally required for use with an operational analyzer.

Bubbler: see absorber.

Calibrating gas: zero air or zero gas containing a known concentration of a pollutant and used for the calibration of an analyzer.

Calibrating solution: a solution used for static calibration of an analyzer, and containing a known concentration of a substance which gives a response equal to that of a known pollutant concentration.

Calibration: the determination of the analyzer response when a series of calibrating gas concentrations are introduced to the analyzer inlet or artificial stimuli are presented to the detector.

Calibration, dynamic: a performance test of the entire analyzer under simulated service conditions in which the response to a calibrating gas over a known concentration range is determined. When reconciled with a static calibration, dynamic calibration also serves to verify 1) the correctness of reagent and sample air flow rates, 2) the efficiency of sample collection, 3) the integrity of the analyzer's plumbing and 4) the quality of any reagents and/or reactants.

Calibration, static: the determination of the analyzer response when artificial stimuli such as standard calibrating solutions, resistors, screens, optical filters, electrical signals, are applied directly to the analyzer detector. It is a performance test of the detection and signal presentation components of the instrument and is primarily applicable to analyzers using colorimetric and conductimetric detectors.

Chemiluminescence (see chemiluminescent under detection methods): an emission of light during chemical reaction.

Collection efficiency: the amount of pollutant measured divided by the amount sampled, usually expressed in percent.

Colorimetry: see detection methods.

Conductimetry: see detection methods.

Contact column: see absorber.

Contactor: see absorber.

Correlation spectrometry: see detection methods.

Coulometry: see detection methods.

Critical Orifice: see orifice

Deadband, Analyzer: the range, in percent of full scale, through which the input pollutant concentration may be varied without initiating an analyzer response greater than twice the noise. (Deadband is commonly applied to servo-systems such as recorders, but can be applied to continuous analyzers as well.)

Detection methods: the techniques used to detect and assay pollutants either directly through physical measurement or indirectly through measurement of a reaction product. Inherent in most detection devices is a comparison system in which the output from the detector is, at some convenient stage, compared to or balanced against a reference quantity such as a known voltage or current, or a color intensity of a reference solution.

Absorption spectrometry (ultraviolet, visible, infrared, and microwave): the detection and assay of pollutants based on the selective absorption of electromagnetic radiation by the pollutants.

Amperometry (not to be confused with coulometry): The detection and assay of pollutants based on the measurement of an electrical current which is the result of a pollutant reacting in an electrochemical cell. The potential and mass transport conditions in the cell are usually adjusted such that the magnitude of the current between electrodes immersed in the electrolyte is proportional to the pollutant concentration.

Chemiluminescent Method: the detection and assay of pollutants based on the emission of light by pollutants during chemical reaction. The intensity of the light produced is proportional to pollutant concentration.

Colorimetry: the detection and assay of pollutants based on the reaction with a solution to produce a colored product having an intensity (or absorbance) proportional to the pollutant concentration.

Conductimetry: the detection and analysis of pollutants based on its reaction with a solution to produce a change in conductance that is proportional to the pollutant concentration.

Correlation spectrometry: the detection and analysis of pollutants by direct comparison and correlation of their spectra with that of known substances.

Coulometry (not to be confused with amperometry): the detection and assay of pollutants by an electrolytic method based on Faraday's Law wherein the quantity of charge (integral of current x time) required for the reaction is proportional to the pollutant concentration.

Emission spectrometry: the detection and measurement of pollutants based on the characteristic spectra emitted when pollutants are excited by heat, radiation, electrical discharge or other stimuli.

Flame photometry: the detection and measurement of pollutants based on the characteristic spectra emitted when pollutants are excited in a flame. Narrow band-pass optical filters are frequently used to isolate a characteristic emission line when measuring a single pollutant.

Fluorimetry: the detection and assay of pollutants based on the characteristic electromagnetic radiation (usually visible light) emitted during exposure of pollutants to radiation having a wave length shorter than that emitted (usually visible or ultraviolet light).

Ionization detector (flame and radiogenic): a device which detects ions produced by passage of a substance through a flame or a region of radioactive emissions. The flame ionization detector is specific for combustible organic compounds. The radiogenic detector may be a highly specific type such as electron capture that responds to electrophilic compounds (e.g., pesticides) or nonspecific such as helium ionization that responds to all gases.

Nondispersive infrared absorption (NDIR): the detection and measurement of pollutants based on their absorption of infrared radiation generated in mixed wavelengths. Spectral specificity is obtained by either a selective detector, optical filters, gas filled interference cells or by pretreating the sample.

Potentiometry: The detection and assay of pollutants based on the measurement of the potential of an electrochemical cell under conditions where the cell potential is determined by the concentration of the pollutant absorbed. With unpolarized electrodes, the electromotive force is usually a linear function of the log of the pollutant concentration in the electrolyte surrounding one of the electrodes in the cell.

Detector (also: sensor, transducer): a device which responds to an input parameter that is a property of, or an effect caused by, a substance being measured. The amount of the substance present is indicated as the deviation of an output parameter from a reference value. The input parameter is often light or other electromagnetic radiation, electrical current or voltage. The output parameter is frequently voltage, current or resistance. Typical detectors are photocells, infrared bolometers and flame-ionization detectors.

Drift, calibration: the change in analyzer calibration which occurs during a stated time period, usually one week, expressed as percent of full scale.

Drift at span: the deviation in analyzer output during a stated time period, usually 24 hours, of unadjusted continuous operation when sampling a span gas concentration equal to some upscale value, usually 80% of full scale. It is expressed as percent of full scale.

Drift at zero: the deviation in analyzer output during stated time period, usually 24 hours, of unadjusted continuous operation when sampling zero air. It is expressed in percent of full scale.

Dry-gas meter (bellows or diaphragm meters): a device which measures the total volume of a gas passed through it without using liquids.

Emission spectroscopy: see detection methods.

Fall time, t_f: see response times.

Flame photometry: see detection methods.

Flow control devices: apparatus for regulating fluid flow, usually by maintaining constant pressure differentials across in-line flow constrictors.

Flow measuring and metering devices: apparatus used to measure and meter fluid flow. Most devices determine flow either by volume displacement or by methods based on the relationship between the pressure differential across an orifice or constriction and the rate of fluid flow through that orifice. Some devices determine total mass transfer by an electrodynamic method. Examples of devices using these principles are:

1) Volume measuring devices - wet test meters, dry test meters, bellows meters, diaphragm meters, etc.

2) Rate measuring devices - rotameters, orifice meters, venturi tubes, pilot tubes, catharometers, anemometers, volume measuring devices used in conjunction with time measurement.

Flowmeter (see also rotameter): any device which measures a rate of fluid flow. In common practice, the term generally refers to a rotameter.

Fluorimetry: see detection methods.

Full scale (see also range): the maximum pollutant concentration measureable for given range, expressed in units such as μg/m^3, ppm, μl/l, %.

Helical column: see absorber.

Helix insert column: see absorber.

Humidity operating range: see operating humidity range.

Impinger: see absorber.

Instrument inlet: the opening through which air sample enters the analyzer, excluding external sample lines.

Interference: an undesired positive or negative output caused by a substance or condition other than the one being measured.

Interference equivalent, IE: that portion of the indicated pollutant concentration caused by the presence of an interferent. It is usually expressed as the ratio, in percent, of the indicated concentration R_i to the amount of interferent C_i present.

$$IE = \frac{R_i}{C_i} \times 100$$

Interferent: a substance or condition other than the one being measured which modifies or perturbs the output of an analyzer.

Ionization detector: see detection methods.

Lag time (initial response time) t_1: see response times.

Linearity: a concept which expresses the analyzer response as a mathematical function of concentration over a specified range. For a linear relationship this function is the equation of a straight line. A non-linear response pertains when the deviation of calibration points about a straight line of best fit suggests non-random scatter and the maximum deviation is greater than a specified percent of full scale.

Lower detectable limit (not to be confused with sensitivity): the smallest pollutant concentration which produces a signal equal to twice the noise. It is usually expressed in concentration units.

Manufacturer: the company or organization which assembled, fabricated or otherwise produced the instrument.

Mechanical absorber: see absorber.

Mobility: a qualitative term used for describing the relative ease with which an analyzer may be moved about. It encompasses the categories: portable, mobile, and stationary. All analyzers can be used as stationary units. Mobile and portable analyzers should have qualities for 1) withstanding the rigors of vibration and acceleration such as occurs during transport, 2) tolerating extremes in environmental temperature variations, and 3) warming-up in less than one hour. Portable units are expected in addition to be lightweight, self-contained, and independent of external utilities such as power, gas, vacuum, and reagents. Instruments intended for mobile operation should be able to meet all performance specifications while in motion.

Model: an identifying name or alphanumeric code other than the trade name assigned by the manufacturer to identify the instrument.

Monitor: see analyzer.

Noise: unwanted, spontaneous, short term variations in analyzer response about the mean output not caused by variations in pollutant concentration. It is usually expressed as percent of full scale (see Figure 10-I).

Noise, audible: see audible noise.

Nondispersive infrared absorption (NDIR): see detection methods.

Operating humidity range: the range of ambient relative humidity (RH) over which the instrument will meet performance specifications.

Operating temperature range: the range of ambient temperature over which the instrument will meet stated performance specifications.

Operating vibration range: the range, in type and intensity, of mechanical vibration in units of distance/time^2 (cm/sec^2) over which the instrument will meet performance specifications. The emphasis is on analyzers designed for portability in field use in motor vehicles and aircraft.

Operating voltage range: the range of power line voltage over which the instrument will meet performance specifications.

Operational period: an indication of the time during which a properly maintained instrument can be expected to function without failure. This may be expressed as a ratio between a specified operating time and the corresponding off-stream, including maintenance, time during that period; as a percent of on-time during a specified operating period; or as an average time between failures (mean failure rate) determined by dividing a specified total operating period by the number of failures which can be expected to occur during that period.

Orifice: an opening through which a fluid can pass and which is shaped to provide pressure-flow characteristics that can be translated to flow rate. At rates approaching sonic velocities, the characteristics are useful for controlling flow (critical orifice).

Output: the final signal, usually electrical (volts, ohms, amperes), produced by the instrument after detection of the pollutant being measured. The signal is a function of the concentration of the pollutant. The function may be linear; if non-linear, it is usually exponential but occasionally it is undefined. (see Linearity) The output is usually fed to a signal presentation device such as a meter, chart recorder, or data processing device (see signal presentation devices).

Packed column: see absorber.

Pollutant: the substance in the atmosphere which the analyzer is designed to detect.

Portable: see mobility.

Potentiometry: see detection methods.

Precision (not to be confused with accuracy): the variability in repeated measurements of the same quantity (e.g., pollutant concentration) expressed as the coefficient of variation, i.e., the standard deviation of the individual results expressed as a percent of the mean.

Primary standard: a substance with a known property which can be defined, calculated or measured, and which is readily reproducible. The standard may be traceable to the National Bureau of Standards or other accepted standards organizations.

Pulse time: see response times.

Range (see also full scale): the nominal minimum and maximum concentrations which the instrument is capable of measuring. Many analyzers provide multiple range selection capability for greater accuracy and ease of interpretation. It is specified by stating the lower and upper pollutant concentrations that can be measured as for example 0 to 1 ppm, 0 to 5 ppm.

Readout: the presentation of the instrument output in an observable display, as for example, with meters, printed numerals or words, light, stripcharts, etc.

Resolution: the ability to separate two closely spaced events in space or time at a signal-to-noise ratio of two expressed as percent of full scale.

Response times: (see Figure 10-I).

Fall time, t_f: the interval between the time to -100% (t_{-100}) and the lag time (t_l). Fall time is not necessarily equal to rise time.

$$t_f = t_{-100} - t_l$$

Lag time (initial response time), t_l: the interval between the time t_o, when a step change (increase or decrease) in pollutant concentration is made, to the time t_i when the instrument indicates a response equal to twice the noise.

$$t_l = t_i - t_o$$

Pulse time: the minimum time a pollutant concentration must persist for the analyzer to register a peak response equal to the pollutant concentration (see Figure 10-I1).

Rise time, t_r: the interval between the time to 100% (t_{100}) and the lag time (t_1).

$$t_r = t_{100} - t_1$$

Time to 95%, t_{95}: the interval between the time t_o, when a step increase in pollutant concentration is made, to the time $t_{95\%}$ when the instrument indicates a response equal to 95% of the step change.

$$t_{95} = t_{95\%} - t_o$$

Similarly, t_{90} corresponds to the time to indicate 90%, and t_{100} the time to indicate 100% of the step change.

Time to -95%, t_{-95}: the interval between the time t_o when a step decrease in pollutant concentration is made to the time $t_{-95\%}$ when the instrument indicates -95% of the step change.

$$t_{-95} = t_{-95\%} - t_o$$

Similarly, t_{-90} corresponds to the time to indicate -90%, and t_{-100} to the time to indicate -100% of the step change.

Rise time, t_r: see response times.

Rotameter (variable area flowmeter): a flow-measuring device that operates at constant pressure and consists of a weight or float in a vertical tapered tube. As the flow rate increases, the float moves upward to a new equilibrium position in a region of larger area, the position being related to flow rate.

Sample: a representative specimen of air collected for the purpose of determining its pollutant content.

Sample, grab: a single sample rapidly collected when expedient. Gaseous grab samples are usually collected in a container or absorbed on a solid or in a solution within one minute.

Sample, integrated: a composite of a series of samples or a continuous flow of sample collected over a finite time period and representing an average sample for that period. Although losses may occur, an integrated sample is often stored for some time before analysis.

Sampling, automated: programmed automatic collection of samples for later detection and analysis.

Sampling, discontinuous: collection of a composite sample during a predetermined total time or until a predetermined total volume has been reached, comprising uniformly timed samples separated by regularly timed intervals. The ratio of on-time versus off-time is stated.

Sampling, random: collection of grab or of integrated sampled at random intervals.

Sampling, sequential: collection of uniformly timed samples that follow each other at regularly timed intervals.

Scrubber: see absorber.

Secondary standard: a substance having a property which is calibrated against a primary standard to a known accuracy.

Selectively permeable membrane: a film which permits certain pollutants in an air stream to diffuse faster than others. It is used for separating or concentrationg those pollutants for subsequent analysis.

Sensitivity (not to be confused with lower detectable limit): the instrument signal output response per unit of pollutant concentration.

Signal presentation devices: devices that are used to convert the analyzer output (the signal from the detection device) to a usable form, such as meters, recorders, digital readout units, computers, and other data acquisition systems (see output).

Signal-to-noise ratio: the ratio of the magnitude of the input signal to that of the analyzer noise expressed as percent of full scale. A ratio of two is usually the smallest value that can be used with confidence.

Space requirements: the area required for safe installation, operation and maintenance of an instrument including allowance for all auxiliary items and equipment such as pumps, reagent containers, etc., and swingout space for cabinet access doors and panels.

Span gas: a calibrating gas containing a pollutant concentration equal to some up scale value, usually 80% of full scale.

Span solution: a liquid reagent used in the static calibration of an analyzer containing a concentration of a substance which gives a response equal to some known pollutant concentration, usually 80% of full scale.

Spanning: adjustment of the instrument output to a selected reading when sampling a span gas or when the detector is subjected to an artificial stimulus such as a span solution, resistor, screen, optical filter, or electrical signal.

Spray jet: see absorber.

Stationary: see mobility.

Stock solution: a solution which contains a known concentration of a standard. This solution may be diluted to provide convenient concentrations for use in analysis.

Telemetry: the conversion of the instrument output into a standardized signal, and transmission thereof to a distant location for interpretation.

Temperature operating range: see operating temperature range.

Time to 95%, t_{95}: see response times.

Time to -95%, t_{-95}: see response times.

Trade name: the name used by the manufacturer or vendor to identify a particular instrument or series of instruments.

Unattended operation: the period of time during which the instrument can be expected to operate unattended within specifications.

Vendor: the independent dealer or distributor of the instrument, instrument supplies, parts and service.

Venturi tube: a tube with a constricted throat formed by a gradually contracting cone followed by a gradually expanding cone used for determining fluid velocity by measurement of differential pressure at the throat as the fluid traverses the tube.

Vibration: an oscillatory velocity or acceleration expressed in units of distance/time^2; e.g. cm/sec^2.

Vibration operating range: see operating vibration range.

Voltage operating range: see operating voltage range.

Warm-up time: the elapsed time necessary after start-up for the analyzer to meet performance specifications when it has been shut down for at least 24 hours. The shortest possible warm-up time (minutes) is desirable for instruments designed for portable field use.

Wet-test meter: a volumetric flow measuring device that measures the total gas volume by entrapping the gas under a liquid in inverted cups or vanes attached to a rotor. The buoyancy of the gas causes rotation of the rotor. The rotation is proportional to the gas volume and is indicated directly on a calibrated dial.

Zero air (see zero gas): air containing 21.0 ± 0.5% oxygen and no substances that will 1) react with the pollutant or interferent gas,

2) alter the test analyzer response or 3) interfere in the referee procedure.

Zero gas (see zero air): an artificial atmosphere containing no pollutants.

Zeroing (also zero adjustment): deliberate translation of the analyzer output or recorded data to a position selected as zero reference while sampling zero air.

Figure 10-I

DIAGRAM SHOWING VISUAL REPRESENTATION AND INTERPRETATION OF TIME DELAYS IN ANALYZER RESPONSE

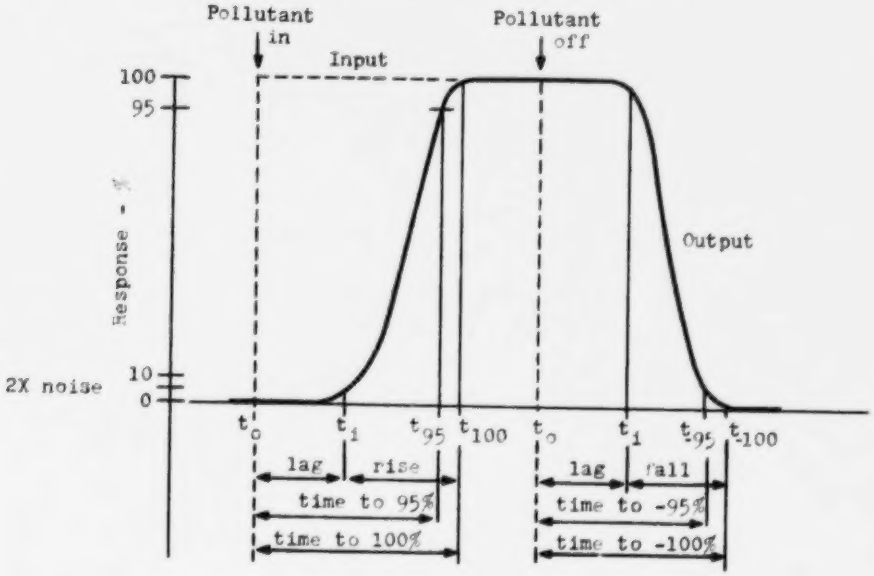
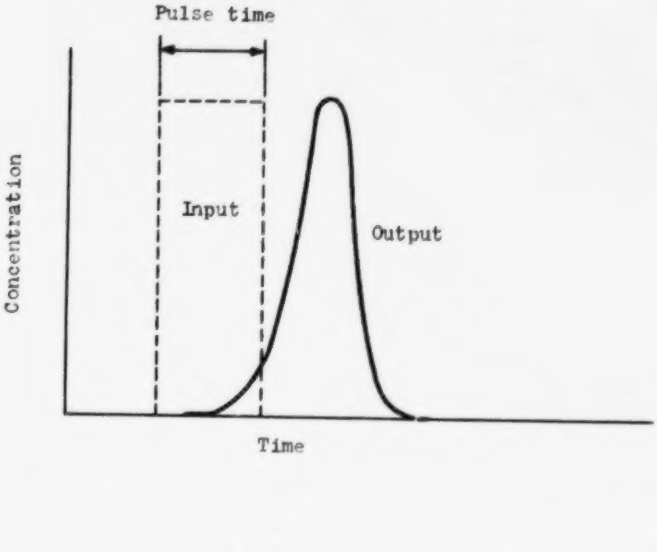

Pollutant in
Pollutant off
Input
100
95
Response - %
Output
2X noise
10
0
t_o
t_1
t_{95}
t_{100}
t_o
t_1
t_{95}
t_{100}
lag
rise
time to 95%
time to 100%
lag
fall
time to -95%
time to -100%

Figure 10-II

DIAGRAM OF PULSE TIME


Pulse time
Input
Output
Concentration
Time

EPA-650/4-74-014

PB-233 048

ERRATA

A GUIDE FOR THE EVALUATION OF ATMOSPHERIC ANALYZERS

(July 1974)

1.	Table of Contents, 3.3:	Correct "maintainance" to read "maintenance".
2.	p 32, para 4.4.3, step 2, line 2:	Between "of" and "any", insert "the slope of".
3.	p 36, para 4.5.3, step 5, line 2:	Between "than" and "4%", delete "of".
4.	p 38, para 4.8.2, step 1:	Between "air" and "record", insert "adjust the instrument baseline to read 5% of full scale and".
5.	p 79, Table 4-IX:	Change "0.874" under CO to "0.870". Change "1.14" under CO to "1.15".
6.	p 108, para 6.2, line 2:	Change "For a 100 liter" to read "For a 10 liter".
7.	p 108, para 6.2, line 3:	Between "reagent" and "and", insert "at a sampling rate of 1.0 liter/min".
8.	p 118, para 6.6.6, step 2, line 1 and 2:	Change lines 1 and 2 to read "Accurately pipet three 20.00 ml aliquots of standard As_2O_3 solution (Item 6.6.4) into 300 ml iodine flasks and...".
9.	p 120, para 6.6.11, line 6:	Change "0.002" to read "0.004".
10.	p 128, para 6.9.1, step 3, line 1:	Before "Rinse", add "Adjust the instrument to the desired measuring range".
11.	p 129, para 6.9.1, step 4, line 9:	Delete "(8.0 ml)".
12.	p 161, para 7.9.1, step 3, line 1:	Before "Mark", add "Adjust the instrument to the desired measuring range".
13.	p 172, para 8.1.2, line 4:	Change "131" to "131,000"; "262" to "262,000".

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ERRATA (continued)

14. p 173, para 8.2, line 4: Change "0.026" to "26"; "26" to "26,200".

15. p 174, para 1, line 4: Change "0.52" to "520"; "26" to "26,200".

16. p 175, para 8.4.3, line 4: Change "errors is important" to read "errors are important".

17. p 175, para 8.5, line 5: Change "0.005 to "5.2"; "2.6" to "2,620".

18. p 179, para 8.6.2, line 1: Change "131" to "131,000"; "262" to "262,000".

19. p 182, para 8.8.2, step 2, line 12: Change "is obtained" to read "obtained is".

20. p 183, para 3, line 2: Change "2.10" to "2100".

21. p 183, para 3, line 3: Change "2.62" to "2620".

22. p 184, equation 2: Change "k" to "P".

23. p 184, equation 3: Change "10" to "25".

24. p 195, para 9.2, line 11: Change "1145" to "1150".

Air and Industrial Hygiene Laboratory
California State Dept. of Health
2151 Berkeley Way
Berkeley, California 94704